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**AN INVESTIGATION INTO THE CHARACTERISTICS
OF POLYURETHANE FOAM FOR MEDICAL
APPLICATIONS PRODUCED USING ADDITIVE
MANUFACTURING TECHNOLOGY**

CHARLES EMMANUEL OPPON

PhD

2016



**An Investigation into the Characteristics of Polyurethane
Foam for Medical Applications Produced Using Additive
Manufacturing Technology**

Charles Emmanuel Oppon

A thesis submitted in partial fulfilment
of the requirements of the
University of Northumbria
for the degree of
Doctor of Philosophy

Research undertaken in the
Faculty of Engineering and Environment

July, 2016

I Abstract

Polyurethane (PU) foam has unique characteristics making it suitable for many applications such as: aeronautics, automotive, building construction, marine, and many household applications. PU's biodegradability, biocompatibility, lightweight, and durability make it suitable for several medical applications. The porous structure of PU foams enables them to be used for lightweight components and for medical applications where the permeability allows nutrients to reach cell growth areas. The foam components are currently mainly manufactured by material removal i.e. subtractive machining or a casting/moulding processes.

Additive Manufacturing (AM) processes (3D printing), build components in 2D layers and have been utilised to manufacture a range of products for many applications including: jewelry, footwear, industrial design, architecture, engineering and construction, etc. The additive processes have the ability to generate internal hollow structures or scaffolds.

The nature of parts produced by AM technologies makes it fit for lightweight products such as aerospace parts, medical scaffolds, etc., in metals and polymers, however the technology has not been used to produce objects using PU as its material, due to the foaming nature of the material when its two base materials (polyol and Diisocyanate) encounter with each other.

This research has undertaken a critical review of PU foaming processes, medical applications, and characteristics of AM technology processes. The effect of resins mixing ratios, temperature, and foaming direction on the physical and mechanical properties of PU foam have been investigated and used as a base to establish a platform for further development.

The research has evaluated the suitability of Additive manufactured PU foam structures for further application such as medical scaffolds by comparing the foams produced using traditional method and have developed an AM production method (In-flight mixing system) for the material (PU). Based on the evaluations, a new technique has been proposed and tested which is able to generate PU 3D structures.

Foam produced by the designed system has average pore size of 689 μ m which will allow the following: the flow of fluid such as blood, diffusion of waste products out of the scaffold, and cell infiltration and can therefore be suggested for the production of medical scaffolds.

II Declaration

I declare that this work has not been submitted for any other award whatsoever and that it is the author's own work, or fully and specifically acknowledged or referenced wherever adapted from other sources.

Signed:

Date: 06/07/2016

III Dedication

This thesis is dedicated to my wife (Harriet) and my three children (Bright, Bertha, and Charles) for their endurance in managing life whilst I was away from them for this study.

IV Acknowledgements

I would like to express my special appreciation and thanks to my Principal Supervisor Dr Philip Mark Hackney, you have been an incredible mentor for me. You really deserve special thanks for your encouragement in making this research a reality. Your advice on both academic and social life in bringing me to this level cannot be quantified. I would also like thank the rest of the supervision team members, Dr Islam Shyha and Dr Martin Birkett for their relentless support in diverse ways in bringing this work into fruition. The Mechanical Engineering technicians deserve appreciation for their assistance in conducting some of the experiments without forgetting those at the Chemistry Department and the SEM lab. Ben Stubb, an undergraduate student deserve credit from me for his tireless support in designing and conducting experiments on the X Y Z Deposition system (FISNAR 4200N brand).

The Minister in charge, Rev Rob Hawkins, the leaders and the entire membership of the Jesmond Methodist Church, Newcastle upon Tyne, where I worship, and Dr Sukumar, leader of the Kingscote Fellowship and the entire members for their encouragement both spiritual and physical. My friends and extended family members who encouraged me in the down periods during the research, you are appreciated.

Special thanks go to my wife, Harriet for carrying out a dual responsibility by taking care of the children alone for the period of this research and the children for missing fatherly love and care for the period.

Ghana Education Trust Fund (GETFund) cannot be left out in appreciation as without them I couldn't by any means been able to afford the program.

Finally, I would say "To God be the glory for the great things He has done".

V	Nomenclature
3DP	Three Dimensional Printing
ABS	Acrylonitrile butadiene styrene
AM	Additive Manufacturing
BiNeo	Bismuth Neodecanoate
CAD	Computer Aided Design
CIJ	Continuous Inkjet
CT	Computer Tomography
DMF	<i>N,N</i> -dimethylformamide
DMLS	Direct Metal Laser Sintering
DNA	Deoxyribonucleic Acid
DoD	Drop on Demand
ECM	Extra Cellular Matrix
EHD	Electrohydrodynamic
e-Mfg	E-manufacturing
FDM	Fused Deposition Modelling
FF	Freeform Fabrication
FT-IR	Fourier Transform Infrared
IJP	Inkjet Printing
IPDI	Isophorone Diisocyanate
JP	Jetted Photopolymer
LENS	Laser Engineered Net Shape
LOM	Laminated Object Manufacturing
LS	Laser Sintering
MDI	Methylene Diphenyl Diisocyanate
MJM	Multijet Modelling
MS	Medical Scaffold
PEG	Polyethylene Glycol
PU	Polyurethane
RIM	Reaction Injection Moulding
RMT	Reactive Metering Technology
RP	Rapid Prototyping
SEM	Scanning Electron Microscope

SL	Stereolithography
SLS	Selective Laser Sintering
TDI	Toluene Diisocyanate
TE	Tissue Engineering
UV	Ultra Violet

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CHAPTER ONE

BACKGROUND TO THE RESEARCH

1.1 Introduction

Additive Manufacturing (AM) can also be referred to as Three Dimensional Printing (3DP), Freeform Fabrication (FF), E-manufacturing, or Rapid Prototyping (RP)^[1]. The technology is a fast growing sector in the manufacturing industry as it has developed from its initial application for rapid prototyping to many functional end products in many fields such as automotive, biomedical, aerospace, jewellery, coin making, tableware, and construction industries^[2]. The technique produces three dimensional solids directly from a digital model or any electronic data source in a layer-by-layer manner^[2-4]. This is different from conventional manufacturing such as moulding where material is injected in a mould to create a part, or the subtractive process (traditional machining technique) which mostly rely on the removal of material by methods such as: drilling, cutting, coining, milling, shaping, etc. from a blank or a bulk material for the part creation^[5]. AM enables multiple parts to be created and assembled simultaneously to receive multiple assemblies at the same time and avoiding hazards associated with assembling^[5, 6]. It is therefore characteristically more efficient and flexible than the conventional manufacturing^[5, 7].

The technology is used for engineering marketing; e.g. prototyping, tooling, direct part manufacturing, maintenance and repair^[7, 8]. AM allows designers and businessmen to evaluate and be satisfied with the feasibility, manufacturability, ergonomics, and aesthetics without going through prototyping which may be costly and time consuming before taking a full scale production^[4, 9]. The benefits of AM are convincing taking into consideration reduction in manufacturing and material costs, reduced process time, and improved performance of product^[10, 11].

AM technology has gained grounds on many manufacturing fields in different sectors as it provides alternatives to traditional methods of production^[5]. One of the major opportunities of AM is its use for medical devices, which includes models and devices employed for the planning and carrying out surgery and custom surgical implants^[12]. Also,

due to its ability to produce custom-fit parts for highly variable joints, amputated limbs, and cavities, the process is used for custom prosthetics and orthotics^[13].

Polyurethanes (Pus) are materials used in many applications such as: aeronautics, automobile, building construction, marine, and diverse household applications^[14]. The use of polyurethane continues to grow as they can be used in areas where other materials do not work; such as corrosion resistance against metals, high impact resistance against plastics, superior load bearing capacity against rubber, etc.^[15] They are among the most versatile construction materials that can be formulated for medical devices^[16, 17]. It is therefore worth investigating the appropriate factors that affect the production and their full usage in order to influence their versatility^[16-19].

Despite the versatile application of AM and wide range use of PU with both arriving at the same point of medical applications, the technology and the material have little or no links in the medical sector due to the production nature of the material^[17, 19].

1.2 Problem Statement

Manufacturing of scaffolds for medical implants can be costly and time consuming using conventional manufacturing process such as machining, casting, moulding, etc. This is because many of these scaffolds have intricate shape and mostly custom built making it difficult to meet the deadline to market. These issues mentioned above are some of the difficulties Additive Manufacturing technology addresses with added advantage of providing better fit. The application of AM for this need has been the manufacturing of metal parts complicated custom implants such as cranial plates and some polymers for other medical applications.

Polyurethane (PU) is a material that has proven to pass the major requirements (biodegradability and biocompatibility), and more especially less costly, light in weight^[15, 20], with allowance for improvements for lightweight medical scaffolds by many researchers. The production of PU has been by pouring the mixture into a mould and machining it to the required shape and size after solidification and curing or spraying onto already built surface. One such application is its use to coat silicone-gel for breast implants.

The application of AM to produce PU foam for expanded industrial applications and possibly for medical scaffolds will require investigations to meet the requirements of

medical scaffolds and also overcome the problems associated with the mixing and dispensing of the material.

1.3 Aim and Objectives

1.3.1 Aim of the Research

The aim of this research is to review the applications of Additive Manufacturing techniques and design a suitable deposition system to manufacture lightweight scaffolds using polyurethane foams for expanded industrial applications and possible use for medical scaffolds. To accomplish this aim, the following objectives were set.

1.3.2 Objectives of the Research

1. Undertake and write a critical review of Polyurethane foaming processes, medical applications and characteristics of Additive Manufacturing technologies.
2. Investigate the effect of resin mixing ratios, temperature, foaming direction on the density, porosity, tensile strength, and compressive strength of PU foam to establish a platform for selection/development.
3. Evaluate the suitability of Additively Manufactured PU foam structures for medical applications compared to traditional produced foams towards developing an AM production method/process.
4. Disseminate research findings via thesis, conferences and journal papers, and presentations.

1.4 Research Methodology

A literature review will be conducted on the basic principles of Additive Manufacturing. Its strength and weaknesses will be looked at, taking into consideration the material characterisations.

The characteristics and requirements of medical scaffold would be researched into and explore the main applications of polyurethanes that are firmly established in the market. Furthermore, the research will investigate into the uniqueness and further development

in medical applications and also, offer improved performance options for PU material fabrication. Experiments will be conducted on the PU by varying the mixing ratio of its main constituents (polyol and diisocyanate) and correspondingly vary the pre-heat temperature as well as conducting various physical tests using the available on-site equipment. Results obtained will be compared for the suitability of PU foam for medical scaffold when its mixing ratio is varied and the pre-heat temperature that will allow free flow (low viscosity) and still maintain the required characteristics of medical scaffolds.

Thorough investigation on the process and AM medical application will be conducted, by laying emphasis on medical scaffolds. The current techniques used in manufacturing medical scaffold by AM will be reviewed and compared to manufacturing of medical scaffold by other processes using PU foam.

The reviewed document and the initial experiments on the PU foam will serve as a guide in designing a system which will be incorporated to the existing 3D printer to dispense PU foam. The designed system will be reviewed and evaluated by creating PU structures which will be analysed dimensionally and the physical performance will be addressed. Results from experimentation will be used to develop an improved analytical model for the mechanical performance of manufactured parts to achieve the aim of 3D printing for its real-world feasibility and application for dispensing PU foam of any kind.

The research methodology will be accomplished by critically following the mapping in Figure 1.1.

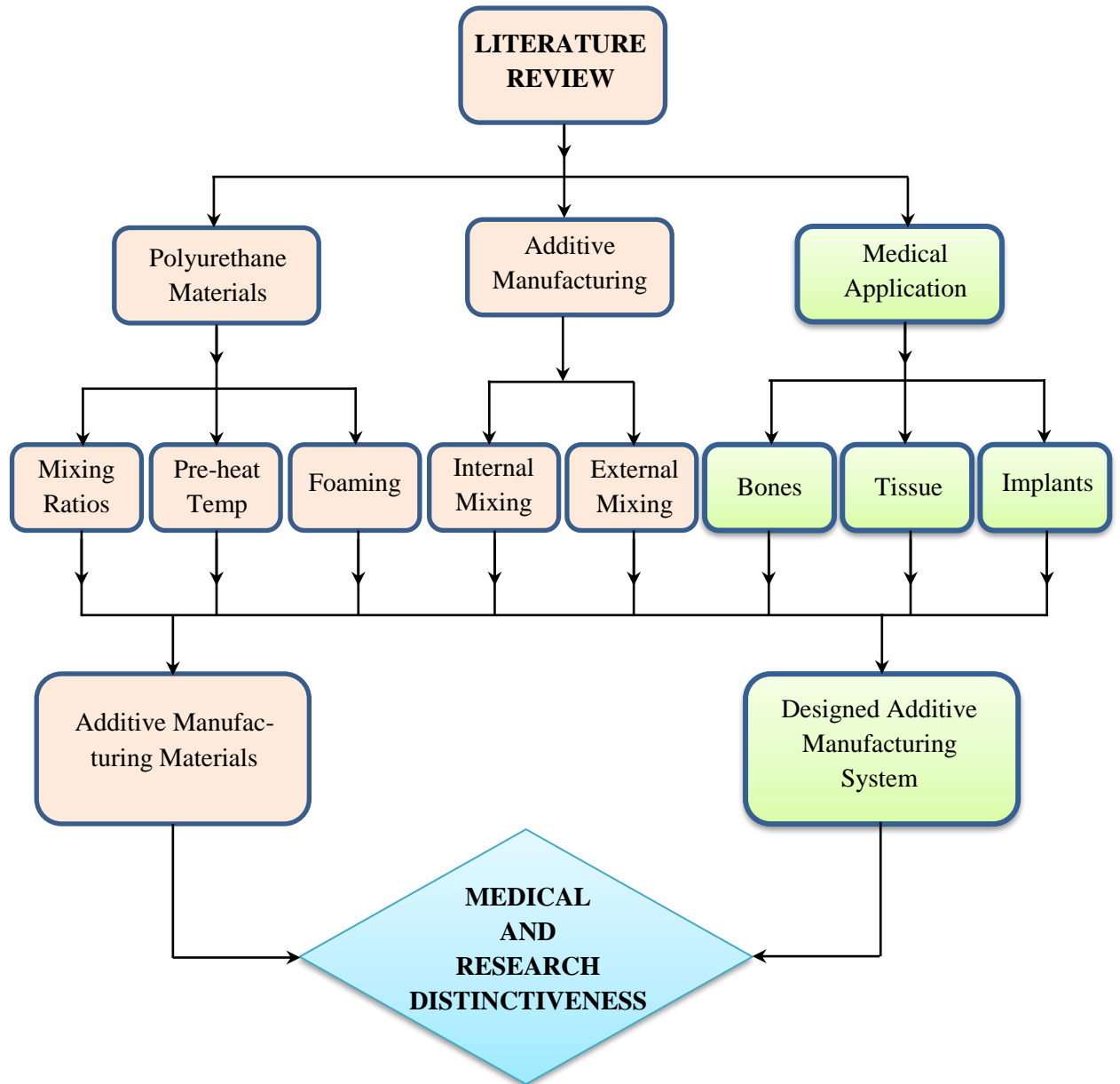


Figure 1.1: Research mapping block diagram

1.5 Organisation of the Thesis

This thesis is structured to cover seven chapters.

Chapter One introduces the industrial applications and economic benefits of Additive Manufacturing technology and polyurethane foams. The non-conformity of AM and PU foam is stated in this chapter which is the problem statement. In accordance with the problem statement, an aim was arrived at, out of which four objectives were set. The

method to follow in achieving this aim and objectives supported by a block diagram is covered in this chapter.

Chapter Two which focuses on the literature review is divided into 3 main sections. Section 2.1 through 2.13 is a documentation of the PU foam constituents as well as its versatile applications including medical. Also, in this group is captured the different conventional methods of producing PU foams. Tissue engineering in general, broken down into medical scaffolds and implants as well as materials used for different medical scaffolds and implants are covered in this range (section 2.14 – section 2.23.4). Section 2.24 through 2.33 documents the principles and applications of AM technologies. The general characteristics (section 2.25) including strengths and weaknesses are documented within these sections. Various AM categories, processes and materials are captured in these sections. Section 2.33 and its subsidiary representing group C looks at AM Inkjet process whose principles of operation could be likened to dispensing of liquids similar to PU foam deposition. Finally, in section 2.34 is the coverage of reactive inkjet printing process used for printing PU foam.

Chapter Three describes the equipment used, experimental plan, and the results obtained from the tests conducted on the PU foam to explore its characteristics for the suitability of producing it using AM with material property adjustment. Screening tests results enabling the selection of mixing ratios for the entire characteristics tests is documented in this chapter. Physical properties test results for different mixing ratios, pre-heat temperature, and foaming directions are investigated, hence, leading to the decision for the design of the deposition system to manufacture PU foam are recorded in this chapter.

Chapter Four covers the first proof of concept using the principle of operation of X Y Z Deposition system (Fisnar F4200N brand) by an attachment to the machine. The results of the tracks printed using the developed attachment to the equipment (proposed system) is also covered in this chapter. Limitations of this system leading to the final design are documented in this chapter.

Chapter Five covers the design of the in-flight system for mixing and depositing of PU foam. It also records the results obtained by using two airbrushes to spray the two main resins of PU foam to mix in-flight on the surface of deposition (built platform). The interface condition of two layers of PU foam is also documented in this chapter, indicating that there is no phase separation.

The chapter again documents the proof of concept by building a PU foam track by the modified/designed system. The limitations of this system are recorded leading to the final design of the attachment to the MakerBot Replicator 3-D Printer to print PU foam.

Chapter Six focuses on the final design of the dispensing unit. The final designed system is thoroughly described in this chapter giving the details of all the sub-systems that constitute it. Results obtained from using the modified/designed system 3D printer to print PU foam substitute are recorded. It also documents the ReplicatorG program written to enable the use the Replicator to print PU foam allowing for dwell period for the laid foam to cure before the next layer is laid.

Chapter Seven concludes the entire investigation with the results obtained from the various experiments. The outcome of the final designed process is documented in this chapter, leading to some recommendations and future work required to obtain the perfection of the designed /modified process.

At the end of the thesis are the appendices consisting of:

- The detailed drawings of the designed nozzle holders,
- Detailed modified ReplicatorG programs that enabled the MakerBot Replicator printer to print the foam blocks,
- Back view of the modified in-flight system, and
- Published journal and conference papers

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This chapter reviews the properties of PU foam and the change that occurs when various chemicals (additives) are combined. Also, the mixing ratio of the main constituents are altered to widen its scope of usage. Its applications in various fields, especially in the medical are reviewed. The properties that make the material suitable for medical scaffolds/implants are discussed.

The Tissue Engineering cycle is generally discussed, taking into consideration the requirements and general properties of medical scaffolds. Processes and conventional materials used in making it have been reviewed.

The chapter also reviews the general principles of Additive Manufacturing technology in comparison with conventional manufacturing processes as well as various categories, materials, and processes of AM.

The principle and applications of Inkjet AM technology which uses material that is liquid in nature in conformity with that of PU base materials has been detailed. A further review of the use of Inkjet AM technology to print PU has been reviewed. Different conventional inkjet technologies have been reviewed, taking into consideration the various methods of producing droplets of inks applied.

2.2 Polyurethane (PU) Materials

Polyurethane is a material belonging to a class of polymers whose characteristics and behaviours make it distinct from other plastics as these plastics are usually created for the manufacture of a particular object. They are class of polymers that display thermoplastic, elastomeric, and thermoset behaviour depending on their chemical and morphological makeup^[18]. PU's are versatile because of their unique chemistry and they have a soft segment that provides flexibility and a hard segment that provides strength^[18]. Pol-

urethane is composed of a chain of organic units which is joined by carbamate links, formed through by step-growth polymerization process, by combining two compounds (diisocyanate and a diol which are monomers) and a chain extender through a chemical reaction. The combination forms a basic material which can have a variation that will remain fairly strong even when it is stretched^[21], or compressed. PU can be in the form of liquid, foam or solid depending on the type of diisocyanates and diol or polyol constituents with each form having its own advantages and limitations^[22]. The severe toxicity issues raised by diisocyanate have raised some noteworthy efforts in recent years to minimize such effects^[23-25]. The polyol which is the backbone, usually a chain extender provides flexibility to the polymer whilst the combination of diisocyanate and the chain extender forms the hard segment, acting as a cross-link and provides it with high tensile strength and high elongation^[20]. PU's are widely-used materials, because of their mechanical and biocompatible properties and can be tuned to suit a particular requirement^[20]. PU's are applied in everyday materials, such as shoe components and other sporting goods, medical devices, and insulation for electric cables^[26]. The automobile industry also has a wide range of application of PU in making components such as dashboards, coatings to avoid abrasions, suspension bushings^[27], etc.

2.3 Formation of Polyurethane Foam

Certain chemicals and aids such as blowing agents are required in the processing of PU foam to ensure sufficient control to obtain commercial products^[28]. During the foaming process, there is an internal reaction that takes place which is controlled by surfactant and this takes place between the non-homogeneous compounds of the system^[18]. The polymer structures are modified by chain extenders or cross linkers, as well as fire retardants, fillers and pigments^[29, 30]. Depending on the PU formulation, catalysts, and application, the reaction typically starts within a few seconds and completes in few minutes. Within this time, the reacting liquid mixture is dispensed into the mould and the combined mixing and dispensing equipment cleaned making it ready for the next cycle of operation^[28, 29]. The exothermic chemical reaction is completed within the mould and the manufactured article can then be taken from the mould after curing and machined to the required size and shape if required for the intended purpose^[28, 29]. The

Table 2.1^[30] illustrates the details of various additives employed in PU foam and their reason(s) for use.

Table 2.1: Table of PU foam additives and their reasons for use ^[30]

Additives	Reasons for use
Catalysts	To speed up the reaction between polyol and polyisocyanate
Cross-linking and chain-extending agents	To modify the structure of the polyurethane molecules and provide mechanical reinforcement to improve physical properties (e.g. adding a polyisocyanate or polyol with more functional groups)
Blowing agent surfactants	To create polyurethane as a foam to control the bubble formation during the reaction and, hence, the cell structure of the foam
Pigments	To create coloured polyurethanes for identification and aesthetic reasons
Fillers	To improve properties such as stiffness and to reduce overall costs
Flame retardants	To reduce flammability of the end product
Smoke suppressants	To reduce the rate at which smoke is generated if the polyurethane is burnt
Plasticisers	To reduce the hardness of the product

2.3.1 Polyurethane Base Material – Isocyanates

Isocyanates used for polyurethane have two or more isocyanate groups on each molecule with the most commonly used ones being the aromatic diisocyanate, toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI)^[31]. The TDI and MDI are less expensive and more reactive compared to isocyanates^[28]. These are normally used in making flexible foams (e.g. slabstock foam for mattresses or moulded foams for car seats), rigid foam (e.g. insulating foam in refrigerators; elastomers such as shoe soles, etc.)^[28]. To reduce the volatility and hence toxicity, decrease the freezing points making handling easier or to improve the properties of the final polymers, diisocyanate are modified by partially reacting them with polyols or introducing some materials^[31].

Where small volumes are required mostly for coatings and other applications where colour is important, aliphatic and cycloaliphatic isocyanates are employed. The PUs that are made with aromatic isocyanates darkens when exposed to light^[32].

2.3.2 Polyurethane Base Material – Polyols

Polyols are classified as either polyether polyols or polyester polyols. Polyether polyols are made by the reaction of epoxides with active hydrogen containing starter compounds and polyester polyols are made by the polycondensation of multifunctional carboxylic acids and hydroxyl compounds^[33]. Polyols can further be classified according to their end use where higher molecular weight polyols (from 2,000 to 10,000) are used to make more flexible polyurethanes whilst lower molecular weight polyols are used for more rigid products^[33]. The low functionality initiators such as dipropylene glycol ($f = 2$), glycerine ($f = 3$) or a sorbitol/water solution ($f = 2.75$) are used by polyols with flexible applications^[28], whereas the high functionality initiators such as sucrose ($f=8$), sorbitol ($f = 6$), toluenediamine ($f = 4$), and Mannich bases ($f = 4$) polyols are used for rigid applications. Many of the properties of polyol are affected by the order of addition and the amounts of each oxide such as, water solubility, compatibility, and reactivity. Polyols that are only made with propylene oxide are terminated with secondary hydroxyl groups and are less reactive than polyols that are capped with ethylene oxide, containing primary hydroxyl groups^[28].

2.3.3 Cross Linkers and Chain Extenders

Cross linkers ($f = 3$ or greater) and chain extenders ($f = 2$) hydroxyl with low molecular weight are amine terminated compounds^[33]. They play an important role in the polymer morphology of polyurethane fibres, elastomers, adhesives, and certain integral skin and microcellular foams^[30]. The elastomeric properties of these materials are derived from the phase separation of the hard and soft copolymer segments of the polymer, such that the urethane hard segment domains serve as cross-links between the amorphous polyether (or polyester) soft segment domains^[34]. This phase separation occurs because the main non-polar, low melting soft segments are incompatible with the polar, high melting hard segments^[34]. The soft segments, which are formed from high molecular weight

polyols, are mobile and are normally present in coiled formation, while the hard segments, which are formed from the isocyanate and chain extenders, are stiff and immobile^[35]. Because the hard segments are covalently coupled to the soft segments, they inhibit plastic flow of the polymer chains, thus creating elastomeric resilience^[34, 35]. Upon mechanical deformation, a portion of the soft segments are stressed by uncoiling, and the hard segments become aligned in the stress direction^[34]. This re-orientation of the hard segments and consequent powerful hydrogen bonding contributes to high tensile strength, elongation, and tear resistance values^[35].

The flexural, heat, and chemical resistance properties is determined also by the choice of chain extenders^[36].

2.3.4 Polyurethane Additive – Catalysts

Even though isocyanates react readily with linear polyol, the rate of reaction decreases rapidly as the size of the substituents on the higher alcohols increases. Thus, catalysts are required to facilitate polyurethane formation. Catalysts for isocyanate and alcohol are mild and have strong bases^[36]. Catalysts used in making polyurethanes can be broadly classified in two main categories namely, amine compounds and metal complexes^[37]. Traditional amine catalysts have been tertiary amines which are selected based on whether they drive the urethane (polyol + isocyanate, or gel) reaction, the urea (water+isocyanate, or blow) reaction, or the isocyanate trimerization reaction (e.g., using potassium acetate, to form isocyanurate ring structure)^[37]. Traditional catalysts can be replaced by catalysts that contain a hydroxyl group or secondary amine, which react into the polymer matrix^[37]. This thereby reduces the amount of amine that can come out of the polymer^[37]. The catalyst and polyols used can be modified by carefully controlling the viscoelastic properties of the material.^[38]

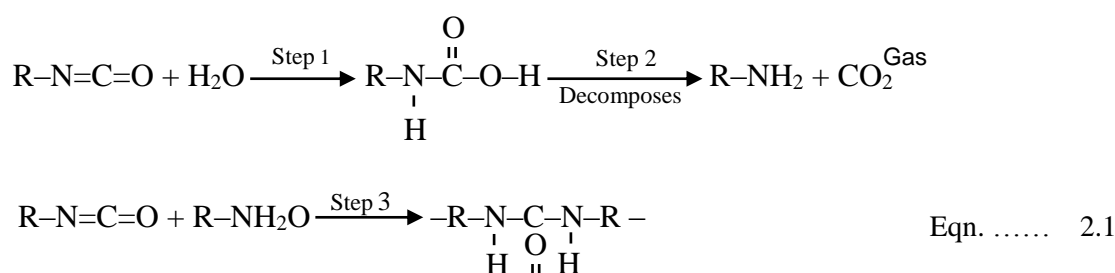
2.3.5 Polyurethane Blowing Agents – Surfactants

Surfactants are additive used to modify the characteristics of both foam and non-foam polyurethane polymers^[37]. They take the form of polydimethylsiloxane–polyoxyalkylene block copolymers, silicone oils nonylphenol ethoxylates, and other organic compounds^[13]. In foams, they are used to blend the liquid components, control

cell size, and stabilize the cell structure to avoid breakdown and sub-surface voids^[37, 38]. In non-foam applications they are used as air release and anti-foaming agents, as wetting agents, and are used to eliminate surface defects such as pin holes, orange peel, and sink marks^[38]. The use of speciality trimerization catalysts create cyclic structures within the foam matrix, giving a harder, more thermally stable structure, designated as polyisocyanurate foams, therefore giving more rigid foam. These properties are desired in rigid foam products used in the construction sector^[37].

2.3.6 Carbon Dioxide Gas Formed by Reacting Water and Isocyanate

The balancing between gelation and blowing is sensitive to operating factors including the concentrations of water and catalyst (Equation 2.1). The reaction to generate carbon dioxide involves water reacting with an isocyanate first forming an unstable carbamic acid, which then decomposes into carbon dioxide and an amine. A substitute urea is achieved by amine reacting with more isocyanate^[39]. Even though the weight percent of water may be small, because it has a low molecular weight, its molar proportion of water may be high, therefore considerable amounts of urea would be produced^[40]. Because urea is not very soluble in the reaction mixture it tends to form separate "hard segment" phases mostly consisting of polyurea. The concentration and organization of these polyurea phases can have a significant impact on the properties of the polyurethane foam^[40].



Without the addition of blowing agents, high-density microcellular foams can be formed by mechanically frothing or nucleating the polyol part preceding the use^[40].

2.4 Production of Polyurethane Foams

Polyurethanes are produced by basically mixing two or more liquid streams to blend and cast in a mould and allowed to foam and solidify to the required shape and size. The polyol stream contains catalysts, surfactants, blowing agents, etc. outlined in Table 2-1^[40]. These two components are denoted as polyurethane system, or simply a system. The isocyanate is commonly referred to as the 'B-side' or as 'iso'^[40]. The blend of polyols and other additives is commonly referred to as the 'A-side' or as 'poly'. This mixture might also be called a 'resin' or 'resin blend'^[40]. The meanings for 'A-side' and 'B-side' are sometimes reversed^[40]. Resin blend additives may include chain extenders, cross linkers, surfactants, flame retardants, blowing agents, pigments, and fillers. Polyurethane can be made in a variety of densities and hardness by varying the isocyanate, polyol or additives. For consistency, this research will refer to Polyols as “A-side” or “part A” and isocyanate or otherwise diisocyanate as “B-side” or “Part B”^{[30] [40]}.

2.5 Health and Safety of Polyurethane Foams

Fully reacted polyurethane polymer is chemically inert (i.e. being inactive)^[37]. It does not readily react with other chemical elements; forming few or no chemical compounds, therefore, having no pharmacologic or therapeutic action^[41]. Polyurethane polymer is a combustible solid and can be ignited if exposed to an open flame^[42]. Because the material is flammable it has to be treated with care (i.e. with flame retardants), and almost all products that are considered harmful^[42, 43]. Additionally, certain chemicals, such as amines, glycols, and phosphate present in spray polyurethane foams present. Substrates used during application of Polyurethane Spray Foam (such as isocyanates) are harmful to human health and therefore special precautions are required during and after this process^[44].

2.6 Manufacturing of Polyurethane Foams

The manufacturing of polyurethane finished goods ranges from small, hand pour piece-part operations to large, high-volume bunstock and boardstock production lines. Irrespective of the end-product, the manufacturing principle remains the same (Figure

2.1)^[45]: to meter the liquid isocyanate and resin blend at a specified stoichiometric ratio, mix them together until a homogeneous blend is obtained, dispense the reacting liquid into a mould or on to a surface, wait until it cures, then demould the finished part^[46, 47].

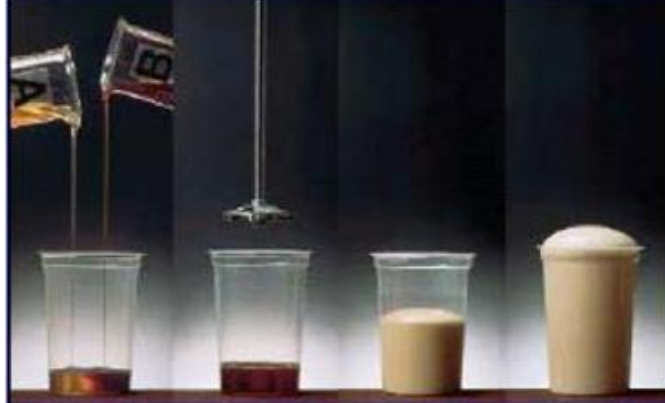


Figure 2.1: Phases in the expansion of PU foam ^[45]

2.7 The Reaction Injection Moulding

The Reaction Injection Moulding manufacturing process (Figure 2.2)^[48] starts with the main polymer resins (polyol and isocyanate) stored in large storage tanks and dispensed by industrial pumps which are large and high pressured. From the storage tanks, the resins are recirculated to a multi-stream mix head on the mould and returns to the storage tanks, forming a continuous loop^[48, 49].

After completion of each part, the piston inside the mix-head withdraws, thereby breaking the continuous loop, and the resins impinge at a high velocity ($\approx 31000 \text{ ms}^{-1}$) to ensure that proper mixture of resins are obtained. The PU thus obtained enters the mould through the after-mixer, which reduces the velocity of the $2500\text{--}2600 \text{ ms}^{-1}$ psi whilst maintaining the properties^[48].

Even though the reaction has a longer production time, it is flexible and cost efficient, wide ranges of part size, design uniqueness, and overall superiority compared to injection moulding, vacuum forming, pressure-forming, and cast moulding^[48].

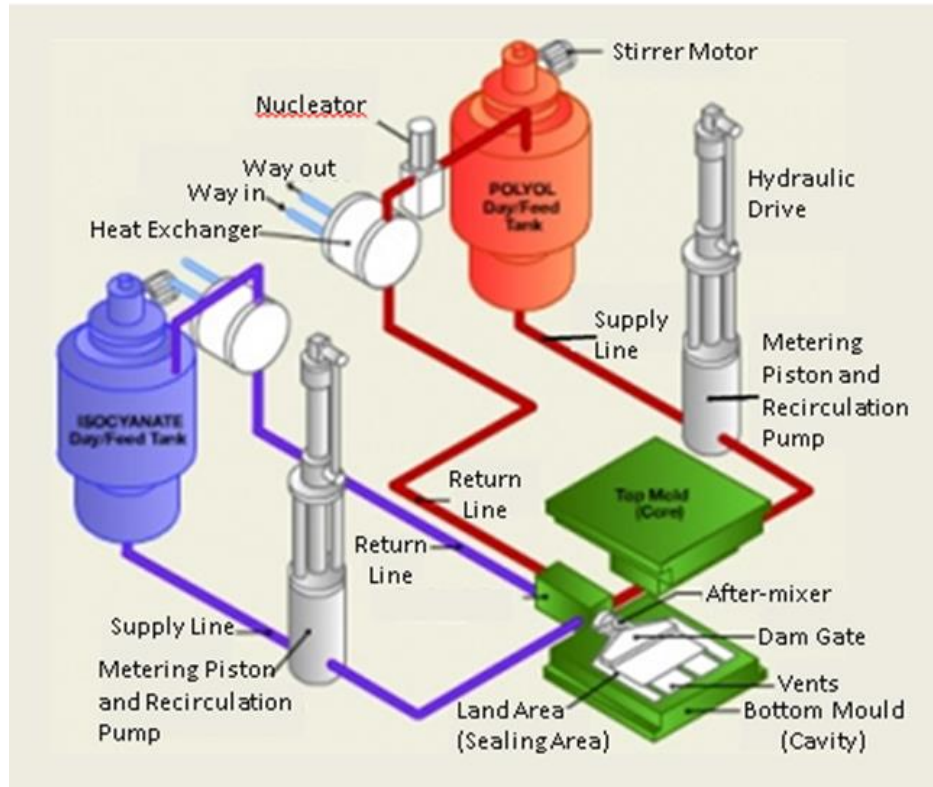


Figure 2.2: Reactive injection moulding (RIM) process ^[48]

2.8 Polyurethane Foam Dispensing Equipment

The use of PU continues to expand as many researchers continue in invention and discovery of new applications therefore, making the dispensing system continue to evolve for new processes and economic demands^[46, 47]. The formula variations of two-part polyurethane elastomer materials, such as polyols and isocyanate continue to grow, hence, their expansion in use by product manufacturers due to their improved performance over other materials^[47]. Although the initial set-up cost may be very high, the use of a meter-mix or dispensing unit even low-volumes that require a steady output of finished part will be appropriate^[47]. Dispensing equipment consists of material holding (day) tanks, metering pumps, a mix head, and a control unit. Some of the equipment has a conditioning or heater-chiller unit added to control material temperature in order to improve mix efficiency, cure rate, and reduce process variability^[47].

The dispensing systems of two-part PU elastomers are designed to be different from other dispensing systems because they have the characteristics to cause meter, mix, and dispense^[46, 47, 50].

2.9 Reactive Metering Technology

The most critical part of the PU dispensing unit is the metering technology^[48]. The two-part metering unit used for this purpose controls the ratio and flow of the polyol and iso materials which are the two main constituents of PU^[26]. Many variables such as flow rate, volume dispensed per application, and mix ratio by volume may modify other properties of the PU^[26]. Appropriate metering technology is of great importance since that determines the performance of the entire dispensing system, the success of the process, and ability of the system to satisfy all dispensing desires, therefore needs to be carefully selected^[44]. If the wrong metering technology is selected, it will mean that the system would need modifications, accessories, or completely new equipment to be able to satisfy the application requirements^[50, 51].

2.10 Meters used for Dispensing Polyurethane Foam

The metering equipment commonly used for dispensing reactive polyurethane can be classified as: “continuous flow” meters and “shot dispense” meters^[52]. Depending on the quantity of material required per the product manufactured, each of these meters has its own essentials for process control and applications that matches its requirements^[50].

Meters can also be classified as either “fixed” or “variable” ratio with each having distinct advantages and disadvantages^[52]. The fixed-ratio meter does not allow changing of the ratio and requires a replacement of a mechanical component, such as a complete meter or component, to change the ratio^[50]. Variable-ratio meters with one drive motor requires a mechanical adjustment to change the ratio^[50]. Variable-ratio meters with dual-independent drive motors (each with their own speed controls) use a simple electronic adjustment in the control panel^[50].

2.11 Uses of Polyurethanes

As mentioned above, PU has a wide range of applications (Figure 2.3). The original reactants, in particular the R^1 and the R^2 groups are the main dependant of the physical properties and the chemical structures of polyurethane^[30]. The properties of final polymer and how polyurethanes are used are influenced by the following characteristics of polyols including: relative molecular mass, the number of reactive functional groups per molecule, and the molecular structure^[30].

Polyurethane foams are not always made to obtain the end product. They are usually produced in the form of large blocks of foam and cut up to the required shape and size for use, such as in cushions, or for thermal insulation^[30]. When cast, the chemical reaction can take place in a mould which may lead to products such as car dash board, car bumper, computer casing, building panel, etc. or it may occur as the liquid reactants that are sprayed onto a surface such as building or coated on a fabric^[30, 53].

The properties of the polymer can be controlled, combined with its density may lead to very wide range of materials enabling PU to be used in very many applications. Table 2.2 illustrates some of the main reasons for choosing PU^[30].

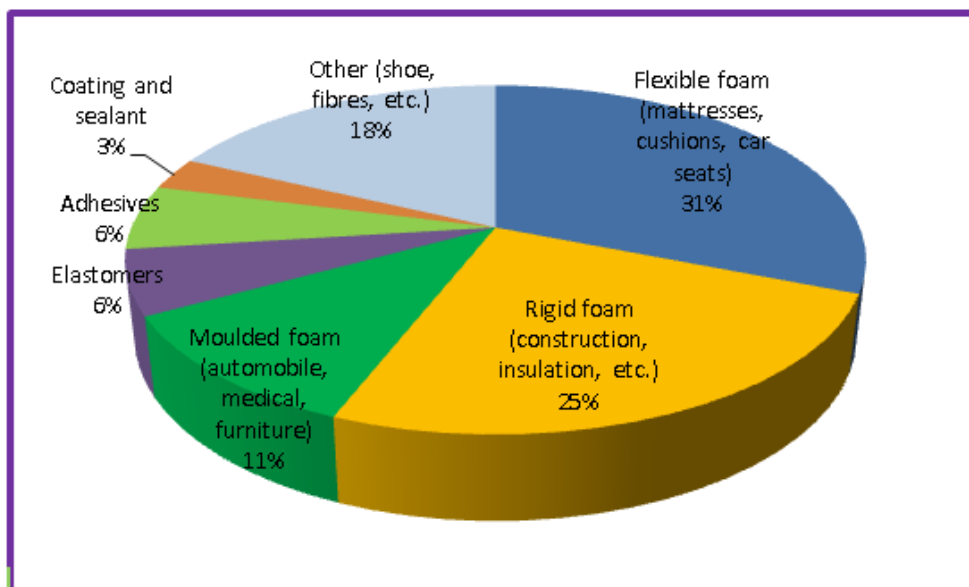


Figure 2.3: General uses of Polyurethane foam ^[30]

Table 2.2: Some examples of main reasons and applications of PU ^[30]

Applications	Properties
Cushioning	Low density, flexibility, resistance to fatigue
Shoe soles	Flexibility, resistance to abrasion, strength, durability
Building panels	Thermal insulation, strength, long life
Artificial heart valves	Flexibility and biostability
Electrical equipment	Electrical insulation, toughness, resistance to oils
Medical implants	Tough, biocompatible, biodegradable, and hemocompatible ^[30]

2.12 Closed-cell and Open-cell Foams

One classification of foams can be either “closed-cell” in which most of the original bubbles or cells remain intact, or “open-cell”, where the bubbles have broken but the edges of the bubbles is stiff enough to retain their shape^[54].

2.12.1 Open-cell Foam

Open-cell foams (Figure 2.4)^[55] are soft and allow the flow of air through it and could be likened to a cushion or the packaging material moulded inside a plastic container to fit a fragile object being transported. The cell walls, or shells of the bubbles, are cracked and air fills all of the spaces in the material. The foam is therefore soft and weak but light in weight^[54, 55]. The insulation value of this foam is related to the insulation value of the calm air inside the matrix of broken cells. The densities of open-cell foams are around 8 kg/m³ to 12 kg/m³^[55].

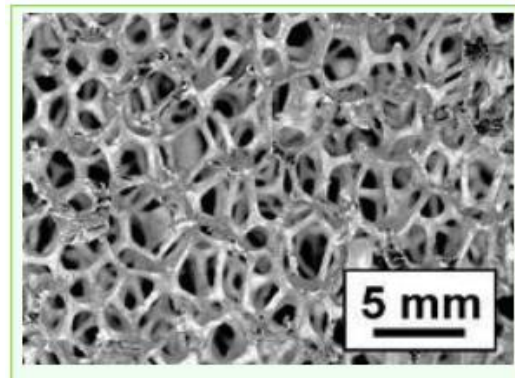


Figure 2.4: Image of open-cell polyurethane foam ^[55]

2.12.2 Closed-cell Foam

The degree of hardness of Closed-cell foam is varied based on its density. A normal closed-cell insulation or flotation polyurethane is between 32 kg/m^3 and 48 kg/m^3 , strong enough to be walked on without major distortion. Most of the cells or bubbles in the foam are not broken (Figure 2.5)^[55]; resembling inflated balloons or soccer balls, piled together in a dense configuration. This makes it strong or rigid since the bubbles are strong enough to withstand a lot of pressure, as inflated tires that hold up an automobile. These cells hold a special gas, selected to make the insulation value of the foam as high as possible^[55].

The advantages of the closed-cell foam compared to open-cell foam include its strength, higher R-value (resistance to heat flow), and greater resistance to the leakage of air or water vapour. The disadvantage of the closed-cell foam is that it is denser, requiring more material, and therefore, making it more expensive. Even though it has a better R-value, the cost per R is still higher than open-cell foam^[55]. The characteristics, such as strength, vapour, control, available space, etc., are the other requirements for the selection of foam for an intended purpose. Both types of foam are commonly used in most building applications. Some are inappropriate in specific applications^[55]. An example is that open-cell foam below grade would typically not be used where it could absorb water, since this would negate its thermal performance as water is a poorer insulator compared to air. Closed-cell foam is preferable where small framing sizes need the greatest R-value per metre as possible^[55].

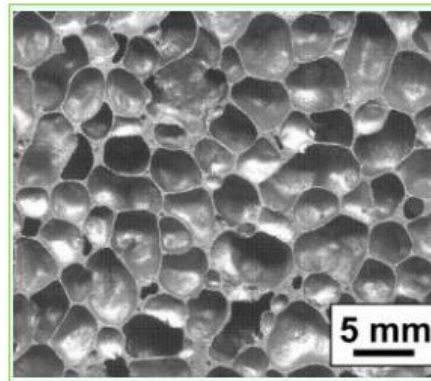


Figure 2.5: Image of closed-cell polyurethane foam^[55]

2.13 Effects of Visible Lights on Polyurethane Foam

Most PU foams, usually made of aromatic isocyanates, comprise of chromophores (that part of a molecule responsible for its colour) that interacts with light. Therefore, in the application of PU coatings, where light stability is a critical factor, aliphatic isocyanates are used^[56]. Exposure of PU foam made of aromatic isocyanates to visible light discolours it, changing from off-white to yellow reddish brown. Generally, it has been accepted that apart from changing the colour from yellow, the ambient^[56] light has little effect on it^[57].

Academic researchers have reported that higher energy UV radiation promotes chemical reactions in the foam, some of which are detrimental to the structure of the foam^[58]. Figure 2.6^[59] shows a photograph of a piece of polyurethane flex moulded that has been discoloured by exposure to UV light.



Figure 2.6: UV Distressed Flex Moulded Foam 800 x 600^[59]

2.14 Tissue Engineering

Tissue engineering (TE) is defined as the study of the growth of new connective tissues, or organs, from cells and a collagenous scaffold to produce a fully functional organ for implantation back into the donor host^[60].

The main aim of TE is to reinstate, preserve, or improve tissue functions that are defective or have been lost by different pathological conditions, either by developing biological substitutes or by reconstructing tissues^[60, 61]. Tissue engineering and regenerative medicine are recent research areas exploring how to repair and regenerate organs and tissues using the natural signalling pathways and components such as stencils, growth factors, peptide sequences, among others, in combination with synthetic scaffolds^[6, 29]. The entire cycle of tissue engineering is shown in Figure 2.7^[29].

Tissue engineering may be classified into three main groups namely: 1) implantation of isolated cells or cell substitutes into organism, 2) delivering of tissue-inducing substances (e.g. growth factors), and 3) placing cells on or within different matrices^[61, 62].

TE is a multi-and interdisciplinary field involving the balancing effort of engineering, chemistry, physics, and biology^[63]. The improvement and development of new materials and processing technologies should therefore be a combined effort of engineers, chemists, physicists, and the biologists^[63, 64]. The issue of new surface treatments and characteristics, techniques, bioreactors, and cell seeding methods should be critically be investigated by the mentioned disciplines^[63-65].

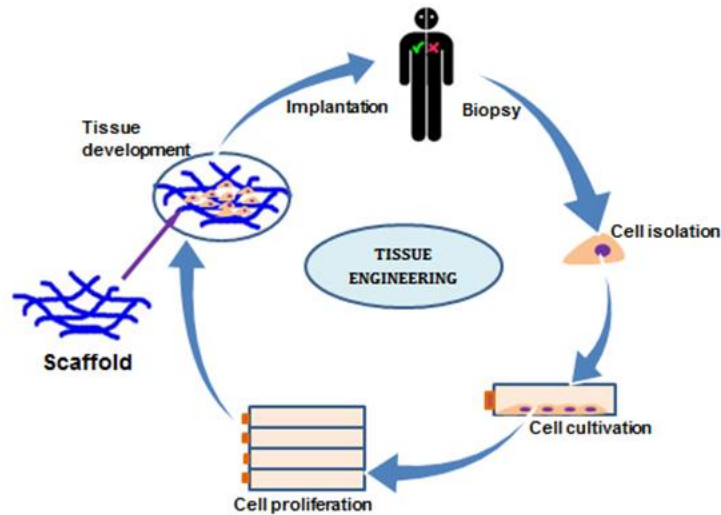


Figure 2.7: Tissue engineering cycle^[29]

2.15 Medical Scaffolds

Scaffolds are defined as three-dimensional porous solid biomaterials^[66] designed to perform all or some of the following functions: (a) promote cell-biomaterial interactions, cell adhesion, and extracellular matrix (ECM) deposition^[66], (b) permit sufficient transport of gases, nutrients, and regulatory factors to allow cell survival, proliferation, and differentiation, (c) biodegrade at a controllable rate that is approximately equal to the rate of tissue regeneration under the culture conditions of interest^[66], and (d) provoke a minimal degree of inflammation or toxicity in vivo^[66]. The scaffold functions as a guiding substrate to the formation of tissue, enabling the arrangement of a structured fibrous tissue across the entire defect, which acts as a secondary supporting network cells^[66, 67].

The design and fabrication of scaffolds are major areas of biomaterial research, and also important subjects for tissue engineering and regenerative medicine research^[61]. During the past two decades there have been many studies done to develop the potential application of scaffold materials for tissue engineering because of the increasing demand of the materials^[61]. Figure 2.8^[68] shows some examples of medical scaffolds made of various materials.

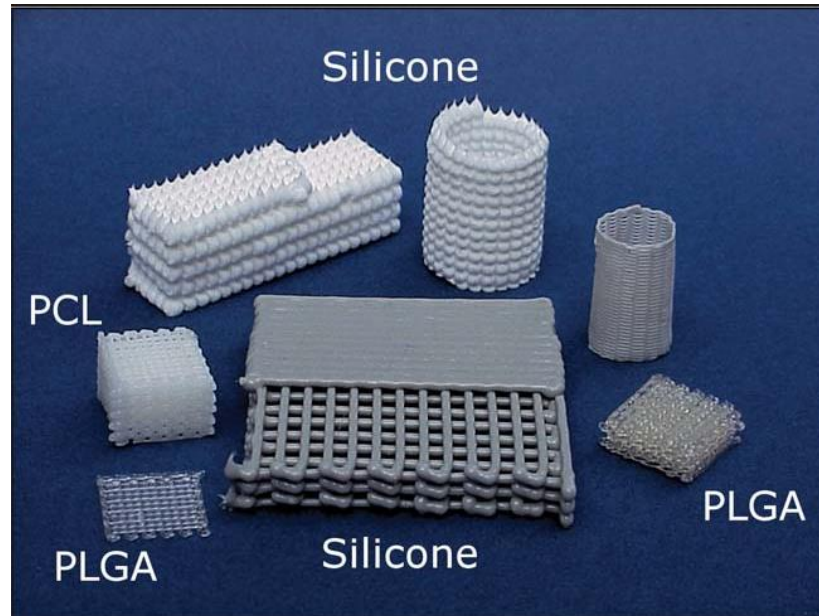


Figure 2.8: Some examples of medical scaffolds ^[68]

2.15.1 Medical Scaffolds - Process of Tissue Engineering

Tissue Engineering starts with some building material (e.g., extracellular matrix, biodegradable polymer), shape it as needed, seed it with living cells and bathe it with growth factors; a structure which is commonly known as medical scaffold^[61, 63]. When the cells multiply, they fill up the scaffold and grow into three-dimensional tissue, and once implanted in the body, the cells recreate their intended tissue functions^[61, 63, 65]. Blood vessels attach themselves to the new tissue, the scaffold dissolves, and the newly-grown tissue eventually blends in with its surroundings^[61, 64, 65].

2.15.2 Requirements of Medical Scaffold

Medical scaffolds play a very critical role in the entire tissue engineering cycle^[69]. In order to fully understand scaffold three-dimensional porous structures and satisfy its intended purpose for tissue engineering,^[65] certain criteria should be fulfilled as enumerated below;

1. The material should be biocompatible and its degradation by-products should be non-cytotoxic.
2. The scaffold must be bio-degradable and should resorb at the same rate as the repair or formation of the tissue.

3. The scaffold must possess a highly interconnected porous network, which is formed by a combination of macro and micro pores that enable proper tissue in-growth, vascularization and nutrient delivery.
4. The scaffold must possess appropriate mechanical properties to regenerate bone tissue in load-bearing sites. Also, the material must maintain its structure reliability during the early stages of the formation of the new bone^[63-65].

2.16 Biocompatibility of Tissue Materials

Biocompatibility is related to the behaviour of biomaterials in various contexts and this is the very first criterion considered by any scaffold for tissue engineering^[69]. The term refers to the ability of a material to perform with an appropriate host response in a specific situation. This means that; the cells must adhere, function normally, and migrate onto the surface and finally through the scaffold and start to proliferate before laying down new matrix^[69].

2.17 Biodegradability of Tissue Materials

Biodegradation is the chemical dissolution of materials by bacteria, fungi, or other biological means^[70]. As mentioned, the aim of TE is to allow the body's own cells to eventually replace the implanted scaffold or the tissue engineered construct after some time. Therefore, the materials used must degrade to allow the cells to produce their own extracellular matrix^[69, 70]. When the biomaterials degrade, they normally release some by-products and these should not be toxic and should be able to leave the body without interfering with other organs^[71].

2.18 Biomaterials in Orthopaedics

Millions of people worldwide (predominantly from the developed countries) above 50 years are affected by bone and joint degenerative problems and is predicted that those affected will be doubled by the year 2020^[72]. In cases of deterioration of natural joint, they require surgery which includes total joint replacement which may be temporal or permanent^[73]. Orthopaedic materials are used to be implanted as constituents of devices

which are designed to perform some biological functions for the substitution or repair of different tissues which may include bone, cartilage or ligaments and tendons, and also guide bone repair when necessary^[63, 67].

Biomaterials are meant to stimulate specific responses at the molecular levels^[74]. The concept biodegradability and bioactivity should be merged, and bioabsorbable material become bioactive and vice versa^[75]. The properties of these materials should merge with their ability to signal and stimulate cellular activity and behaviour^[75]. Scaffolds may be biologically derived from human or animal tissues, synthetically derived from polymers, or metallically derived from metals such as titanium^[75].

2.19 Mechanical Properties of Medical Scaffolds

Mechanical properties are normally used to classify or categorize and identify materials. The most common properties considered are strength, ductility, hardness, impact resistance, and fracture toughness. Most structural materials are anisotropic, which means that their material properties vary with orientation^[76, 77]. Mechanical properties of medical scaffolds are required to be consistent with the anatomical site as planted^[76]. It should be strong enough (not at the expense of other properties) to allow surgical handling implantation. One of the major challenges that confronts scaffolds production is the bone or cartilage having the required mechanical properties^[76-78]. Another big challenge associated with the design of orthopaedic applications scaffold design that healing rate varies with the age of the patient. O'Brien et al, in their research indicated that the fracture in young individuals normally take about six weeks to heal to the point of weight-bearing with a complete mechanical reliability whilst that of an elderly takes a longer period^[69]. A lot of materials have been produced that did not retain their porosity even though they had good mechanical properties^[69]. In the design of medical scaffold, careful balance should exist between the mechanical properties and should be porous enough to allow cell infiltration and vascularization which is key success of any scaffold^[69, 79].

2.20 Architecture of Medical Scaffold

Medical scaffolds play a very important role in cartilage tissue engineering as it guides the formation process of tissue substrate. Its architecture and composition are important parameters, therefore, should be given critical consideration during its design^[67]. In order to ensure cellular penetration and adequate diffusion of nutrients to cells within the construct and to the extra-cellular matrix formed by these cells, scaffolds should have an interconnected pore structure and high porosity^[76]. Also, a porous interconnected structure is required to allow diffusion of waste products out of the scaffold, and the products of scaffold degradation should be able to exit the body deprived of interference with other organs and neighbouring tissues^[69, 80]. Again, in the design of a scaffold, there is a critical range of the pore size which may be rejected outside that range and may vary depending on the cell type and the specific application^[80].

2.21 Manufacturing of Medical Scaffold

Medical scaffolds are manufactured using different techniques, each of them having its own advantages and limitations with variable mark of success^[80]. Porous scaffolds which are composed of biodegradable polymers is an example that have found extensive use in the engineering of several types of tissues^[75, 76]. Numerous tissue engineering schemes are applied; an example is conductive approaches that use conductive and inductive substrates for absolute implantation for in-vivo or cell-based approach with scaffolding materials as three-dimensional substrates which is used for in-vitro cell seeding followed by transplantation^[81, 82].

Medical Scaffolds are fabricated on a framework that helps to regulate the scaffold interconnectivity and pore size which must be removed after the scaffold is formed. The current approaches are accompanied with some difficulties which are; regulating the scaffold interconnectivity and pore size and difficulties in removing the framework material after forming the scaffold^[76, 81]. One major criterion to consider for a particular scaffold to become clinically and commercially viable is that it should be cost effective and possible to scale-up from making one construct at a time in a research laboratory to a small batch production^[83]. This is one of the key advantages of Additive Manufacturing. Prototypes in manufacturing process ensure good manufacturing practice (GMP)

standard and determining how a product will be delivered and made available to the clinician are very vital for the successful translation of tissue engineering in the clinic. This determines the storage method of the tissue engineered construct^[84].

2.22 Properties of Biomaterials

Biomaterials must be compatible with the body, and there are often issues of biocompatibility which must be resolved before a product can be placed on the market and used in a clinical setting. Because of this, biomaterials are usually subjected to the same requirements as those undergone by new drug therapies^[85-87]. Biomaterials can be obtained from nature or could be manufactured using a chemical approach in the laboratory^[85]. The chemical approach may make use of metallic component, polymers, ceramics, or composite materials. Biomaterials are often used and/or modified to suit medical purposes comprising the whole or part of a living structure or biomedical device which augments, performs, or replaces a natural purpose^[85-87]. It is regularly used in dental applications, surgery, and drug delivery^[85]. The following are some of the applications of biomaterials which will not be fully discussed in this research.

- Joint replacement
- Bone plates
- Bone cement
- Artificial ligaments and tendons
- Dental implants for tooth fixation
- Blood vessel prostheses
- Heart valves
- Skin repair devices (artificial tissue)
- Cochlear replacements
- Contact lens
- Breast implants
- Drug delivery mechanisms
- Sustainable materials
- Vascular grafts
- Stents

- Nerve conduits
- Surgical sutures, chips, and staples for wound closure^[85].

Materials currently used for load bearing applications including dental replacement and bone joining or replacement for medical and clinical applications^[88] may include:

1. **Metals and alloys**, such as: stainless steel, titanium, nickel, magnesium, Co–Cr alloys, Ti alloys^[88, 89],
2. **Ceramics**, such as: zirconia, bioglass, alumina, hydroxyapatite^[88, 89], and
3. **Polymers**, such as: acrylic, nylon, silicone, polyurethane, polycaprolactone, polyanhydrides^[88, 89].

2.23 Bone Grafting

Bone grafting is the procedure used by surgeons to replace missing bone for the repair of bone fractures that are very complex and poses significant health risk to patient, or fail to heal properly^[90]. Generally, bones have the ability to regenerate but will require a small space, usually a fracture, or some form of scaffold to do so. Bone grafts can be used prior to placement of implant or simultaneously^[90].

2.23.1 Types of Bone Grafts

Bone grafts may either be autologous, where the bone is harvested from the patient's own body; allograft, where cadaveric bone is usually obtained from a bone bank; or synthetic, which is often made of hydroxyapatite or other substance which occur naturally and biocompatible having similar mechanical properties as bone^[91]. Bone grafts are mostly required to be reabsorbed and replaced by the natural bones as they heal usually in few months^[91].

The successful bone grafting includes: guiding the reparative growth of the natural bone (osteoconduction)^[91], encouraging undifferentiated cells to become active osteoblasts (osteoiduction)^[91], and living bone cells in the graft material to contribute to bone remodelling (osteogenesis)^[91].

2.23.2 Case study – Titanium Bone Implants

A portion of human bone was replicated using titanium to demonstrate that the complex surface of a real bone could be recreated in a structural implant material^[92]. One of the major limitations of bone implants is the mismatches between implants and real bone which often cause stress concentrations sometimes resulting in premature implant failure^[92]. The use of Selective Laser Sintering (SLS) process of AM technology produces a titanium piece which is an exact duplicate and therefore fit the patient's bone structure exactly with a longer service life. In this study, the University of Texas at Austin produced an accurate titanium replica of the ball section of a human femur bone (Figure 2.9) using SLS process of AM^[92]. Because of a major limiting factor in titanium processing being its extreme reactivity with many atmospheric elements, especially at elevated temperature and to avoid contamination of mould for the titanium casting, the ball was produced using SLS^[92].

The processing steps used is summarised as follows:

1. Acquiring a very detailed 3D representation of the outer surface of a human femur
2. Generating a 3D model of the bone that could be manipulated digitally
3. Creating and modifying a 3D digital mould of the ball section of the femur
4. Constructing and post-processing zirconia mould material
5. Constructing and post-processing zirconia mould material
6. Creating a usable bone mould and casting at a titanium foundry
7. Evaluating the integrity of the finished titanium pieces^[92].



Figure 2.9: Titanium bone implant ^[92]

2.23.3 Load Bearing Improvement of Titanium Bone Implant

Researchers at the Fraunhofer Institute for Manufacturing and Advanced Materials in Dresden have developed a titanium-based substance for a new generation of implants^[92]. The new material developed is porous and makes implants less stiff than the conventional ones and also promotes in-growth into surrounding bones^[92]. This was developed through a powder-metallurgy-based moulding process^[92].

2.23.4 Mechanical Properties of Bone

Even though bone is an organic material, it is often considered the same way as artificial engineering materials. The nature of the synthesis of bone makes it likely to show many variations in its properties than engineering materials^[93]. These factors may include:

- Age
- Gender
- Location of bone in the body
- Temperature
- Mineral content in the bone
- Amount of water present
- The type of effect (disease, such as osteoporosis)^[93].

The above variables may be reliant on each other to some extent, such as the variation of mineral content according to the location of the bone in the body, and also the patient's age. Human bones characteristically reduce in density with age and therefore the reduction of strength, making it susceptible to fracture^[93].

Because of the stated variables, measured properties of bones given in tables are usually average, with quite a significant spread in the data^[94]. Also, as the structure of bone is anisotropic, its mechanical properties should be considered in two orthogonal directions:

1. Longitudinal: which is in the direction of loading being parallel to osteon alignment
2. Transverse, which is at right-angles to the long axis of the bone^[94]

2.24 Additive Manufacturing

Additive Manufacturing (AM) or Three Dimensional (3D) printing is a group of techniques for making three dimensional solid objects or assembly from a digital model^[9]. This is achieved by additive processes, where an object is created by laying down successive layers of material until the final object is obtained^[95]. This is considered as distinct from the conventional manufacturing such as moulding where material is injected into a mould to create a part^[5], or the subtractive process (traditional machining technique) which mostly rely on the removal of material by methods such as: drilling, cutting, coining, milling, shaping, etc. from a blank or a bulk material for the part creation^[5, 6, 96]. AM technology is used in jewelry, footwear, industrial design, architecture, engineering and construction (AEC), automotive, aerospace, dental and medical industries, geographic information systems, and many other fields^[97]. The complexity and the performance of parts produced by the AM are enhanced by the emergence of Multiple Material Additive Manufacturing (MMAM) technology^[98]. With these technologies, material compositions could be varied to improve the parts' performance^[98, 99].

2.24.1 General Additive Manufacturing Principles

Even though several AM processes exist, they are all based on the same basic principles with various limitations such as: build speed, interlayer adhesion, materials and support structure^[100].

The process (Figure 2.10) starts by arranging the parts to be formed within a specified build area, and determining the suitable build direction of the part to be built^[101]. The factors that influence the orientation of the part to be built are: dimensional accuracy, clarity of detail, support and support removal, and build-time^[101, 102]. Once orientation has been decided, the parts all run through "slicing" program, cutting the parts into "Z" layers. The "slice file" is then transferred to one of the AM machines, where the parts are then formed layer by layer^[100, 102, 103].

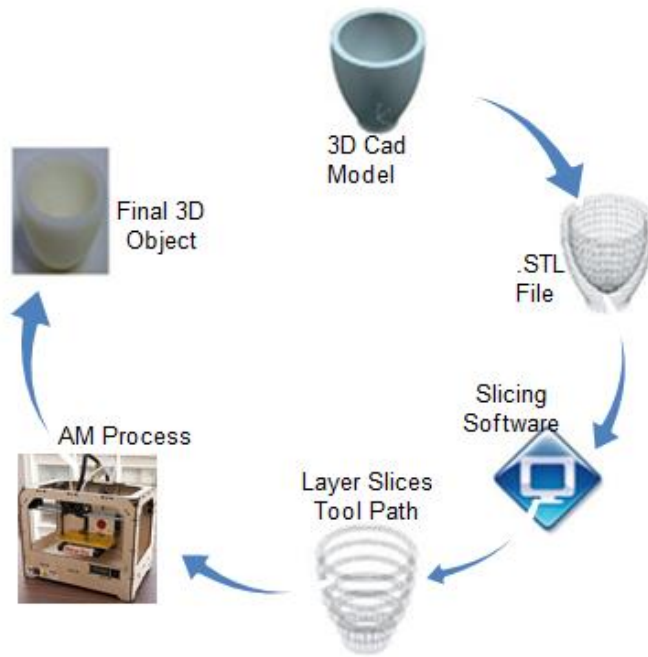


Figure 2.10: General Additive manufacturing process cycle ^[100]

2.24.1.1 Modelling

Additive manufacturing takes a computer generated design from Computer Aided Design (CAD) software, or obtained from laser scanning, Computer Tomography (CT), Magnetic Resonance Imaging (MRI) and Mathematical modeling software and stores it in stereolithography (stl.) file format^[2, 104] which is the Rapid Prototyping industry's standard data transmission format, that approximates the surfaces of a solid model with triangles^[5]. The file is then imported into slicing software which "slices" (Figure 2.11) them into numerical cross-sections and orient appropriately in order to define the best possible tool path for the printer which then creates the object through selective placement of material^[3]. The AM machine used determines the material or binding material ^[2, 105]. Choosing the appropriate building direction is essential as it can change specifications of the object such as quality, cost and lead time^[104].

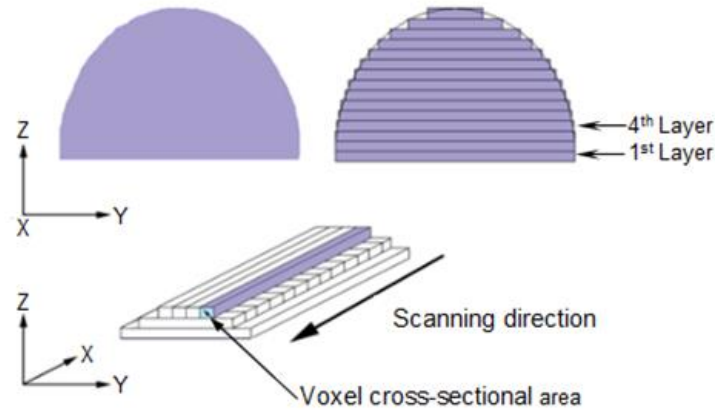


Figure 2.11: Additive manufacturing slicing ^[104]

2.24.1.2 Printing

The machine reads the design and then deposits the liquid, powder, or sheets of metal successively depending on the type of process building the model from a series of cross sections as illustrated in Figure 2.11. According Wohler in his 2009 report, typical layer thickness of the printer is around $100\ \mu\text{m}$ ($0.1\ \text{mm}$)^[97], but recent publications have shown that some machines such as the *Objet Connex* series can print layers as thin as $16\ \mu\text{m}$ ^[106]. The particles (3D dots) are around 50 to $100\ \mu\text{m}$ (0.05 – $0.1\ \text{mm}$) in diameter^[10].

2.24.1.3 Finishing

Because of the intrinsic resolution of AM printer which is low and may be appropriate for some applications, parts produced by AM that requires higher resolution may have to be produced oversize and a higher resolution process such as CNC machining be used to remove the excess material^[2, 5].

2.24.2 Characteristics of Additive Manufacturing

AM technologies have some characteristics which some are strengths and others weaknesses or limitations:

2.24.2.1 *Speed*

Additive Manufacturing has been described as “rapid” processes due to its short build times as compared to conventional manufacturing^[107-109]. Lead time in completing parts made by AM is greatly reduced as no custom tooling needs to be developed^[110]. The use of AM as rapid prototyping tool has enabled it been used for fast iteration, and has considerably reduced time for new product to the market^[107, 110, 111] even though speed per specific part is low compared to other manufacturing processes^[5, 111].

2.24.2.2 *Part Complexity*

AM technology allows engineers to lay emphasis on design or optimize functions rather than machinability to internal features and surfaces that are extremely complex, which may give form of apparently geometries that are impossible and almost every conceivable shape^[112, 113].

2.24.2.3 *Parts Produced Assembled*

With AM, parts that would have to be built in bits and assembled as in the case of conventional manufacturing can be created as one piece, thereby assembling time and storage of individual parts are saved^[7, 114]. An example is an assembled adjustable spanner shown in Figure 2.12 which was produced using the selective laser sintering process^[115].



Figure 2.12: Assembled part produced by AM ^[115]

2.24.2.4 *High and Low-Volume Production*

Review conducted by this research has shown that certain traditional techniques such as moulding and casting can be less expensive for mass production of polymer products but AM process can be faster, flexible and cheaper when producing parts in small quantities^[8, 116]. An example is the surgery planning and custom design for replacement of parts such as; knee, pelvis, and hip joints^[117], building a pattern tool for moulding or casting, building a model as replica of an expensive object^[118].

2.24.2.5 *Lighter Products*

Parts produced by AM can be manufactured hollowed out (internal scaffold), thereby making the product light in weight whilst still maintaining the required strength, and also, reducing the cost of material as less material would be used^[119, 120]. These lighter products when fitted into final products may save energy across its lifespan^[5, 102]. Also, when parts of a moving object such as aircrafts are made by AM process, less energy is required to move, hence reducing cost of fuel^[39, 121].

2.24.2.6 *High Accuracy and Surface Finish*

Currently, AM processes cannot match the precision and finishes offered by some traditional machining such as CNC machining, honing, lapping, etc.^[122]. As a result, parts produced by Additive Manufacturing process may require secondary operations depending on their required surface finish and its intended use^[5, 39, 122].

2.24.3 *Material Properties*

While AM can utilize various material types, individual material options are somewhat limited^[121]. As a result, materials that offer certain desirable properties may not be applicable for AM. Also, due to the fabrication methods, the properties of the final part may not meet certain design requirements^[61, 121, 123].

2.24.4 Material Costs

Although in some of the AM processes such as Selective Laser Sintering, only the build material required to build the part is used, raw materials may be very challenging, such as utilise powderised metals. Also, the current prices of materials used in additive processes are far greater than more commonly used materials for other processes^[61, 124, 125].

2.25 Multidisciplinary Nature of Additive Manufacturing Technology

Although there are limitations in the use of Additive Manufacturing Technology, it still possesses a wide range of multi-disciplinary culture of materials and application^[126]. Figure 2.13^[127] shows the range of applications and materials used. More research are been conducted to expand the applications and materials used^[126].

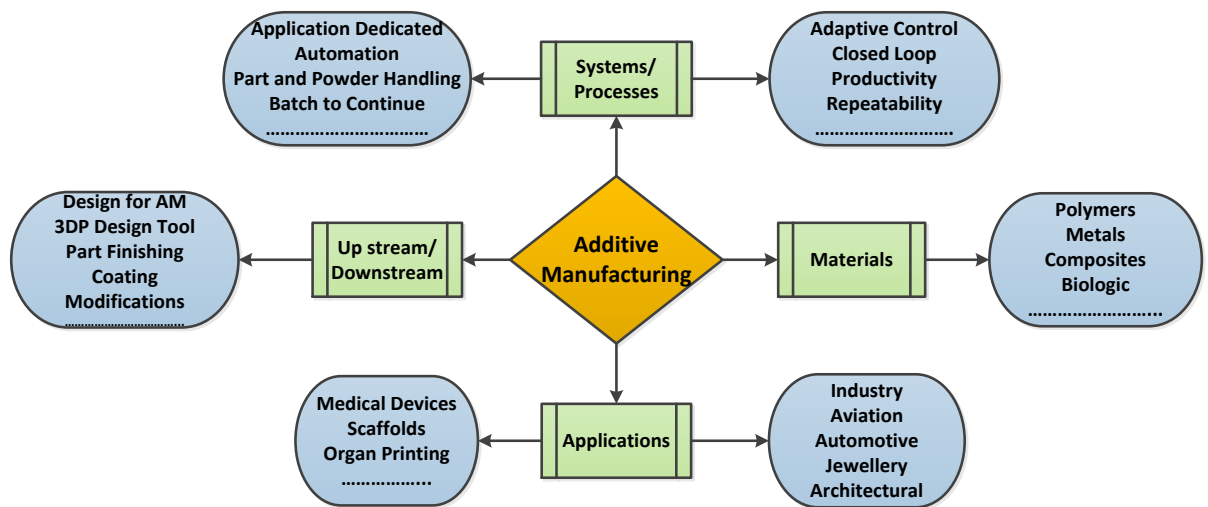


Figure 2.13: Block diagram showing the multi-disciplinary nature of AM technology ^[127]

2.26 Functional Parts and Tools by Additive Manufacturing

2.26.1 Introduction

Even though many manufacturing industries are using the AM technology to solve a lot of complicated problems with material requirements ranging from plastics or ceramics to steel or titanium, the technology has not been able to solve every problem confronting the manufacturing sector^[107, 128]. The technology is therefore not considered as complete substitute to conventional processes but rather suitably considered as their complements^[107, 128, 129]. The technology cannot produce parts in a wide enough range of materials to the entire spectrum of requirements of industry and science^[105, 107, 129].

AM technology is used in two ways to make useful items; i.e. *Direct* and *Indirect* or *Secondary Processes*^[1].

2.26.2 Direct Processes

2.26.2.1 Plastic Parts

With other processes of AM technology in use, some of the most significant ones thought to be for end-use directly fabricated products are Laser Sintering (LS)^[2, 13, 124], thermoplastic extrusion such as Stereolithography (SL)^[130], or Fused Deposition Modeling (FDM)^[1, 5, 131]. Laser sintering extends its fabrication process to a wide range of engineering plastics such as glass-filled nylon, polystyrene and PEEK^[132, 133]. Examples of the thermoplastic extrusion materials that are fabricated by laser sintering may include: ABS, polyphenylsulfone, polycarbonate, polyester, among others^[133, 134]. Parts produced by these processes possess higher strength and some added properties that are found currently in photopolymers^[135, 136]. Factors influencing the mechanical properties of parts produced by AM process build part are: the direction, and the layered fabrication process itself^[135].

2.26.2.2 Metal Parts

Additive manufacturing processes that most often directly fabricate metal parts are Selective Laser Sintering (SLS)^[61, 137, 138], Direct Metal Laser Sintering (DMLS)^[137, 139, 140], or Laser Powder Forming^[61, 137]. Where necessary, porosity may be reduced by sec-

ondary metal infiltration and secondary process applied when required^[61, 138, 139, 141] to improve the surface finish.

2.26.3 Indirect or Secondary Processes

Despite the significant advancement in the growth of materials in AM technology processes, its unmeasurable display of application requires that there is always the need to transfer AM fabricated parts into another material^[139].

- The application
- Volume of parts to be produced
- Final material and accuracy requirements
- The availability of a particular additive process.

Figure 2.14 shows Roadmap to useful Parts & Tools by Additive Fabrication that aids to find a way through the terminology and technologies^[139].

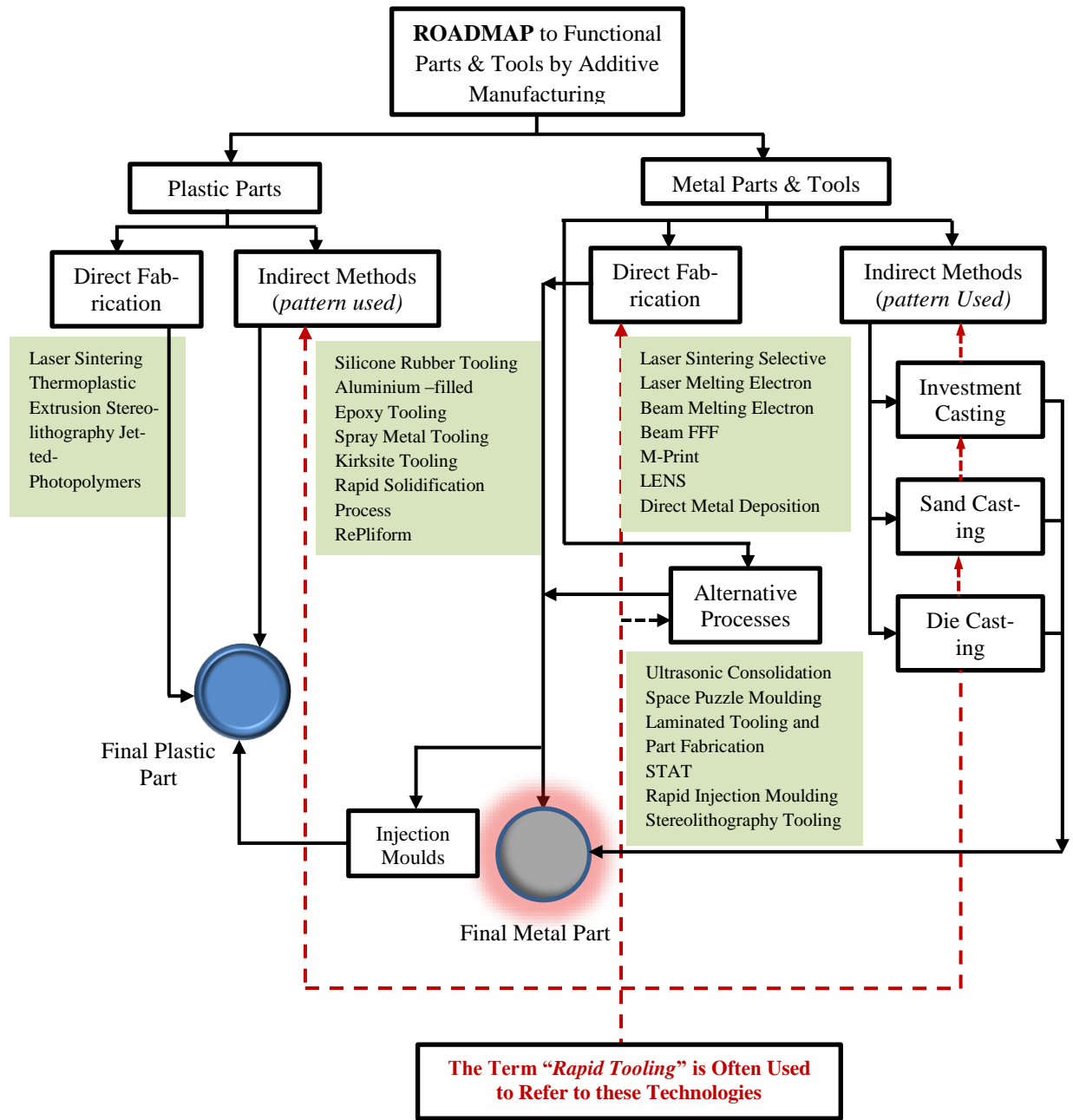


Figure 2.14: Roadmap to functional parts & tools by additive^[139]

2.27 Additive Manufacturing Categories, Processes, and Materials

Even though there are a number AM technology processes available, researchers continue to work to add more of the processes^[5]. The processes can be grouped into categories and differ in the way layers are built to create parts, and particular material application^[135, 142]. While some methods use softening or melting of material to produce the

layers, others lay liquid materials and then cure with different processes^[142, 143]. Others also use thin layers of materials such as paper which are cut to shape and joined together^[142, 144].

Despite the uniqueness of the various AM processes, with varying characteristics, each method has its strengths or advantages and weaknesses or disadvantages^[118, 144, 145]. These lead to a number of manufacturers a choice between paper, polymer, metal, etc. in the form of liquid, powder, or solid^[134] for an object emerging from these materials^[118, 121, 146].

2.27.1 Liquid-Based Process

These processes characteristically use photopolymer resins and cure selected portions of the liquid vat to form each layer^[147]. The most common liquid based process is stereolithography^[148] (Figure 2.15). Parts produced by this process have high accuracy with appearance similar to moulded parts, but with poor mechanical properties that sometimes worsens overtime. Others include jetted photopolymer^[149] and Inkjet printing^[147] which may be single or multiple jet^[150].

For example, the basic principle of Jetted Photopolymer is the photopolymerization, which is the process where a liquid monomer or a polymer converts into a solidified polymer by applying ultraviolet light which acts as a catalyst for the reactions; this process is also called ultraviolet curing^[151]. It is also possible to have powders suspended in the liquid like ceramics^{[147, 148] [150]}.

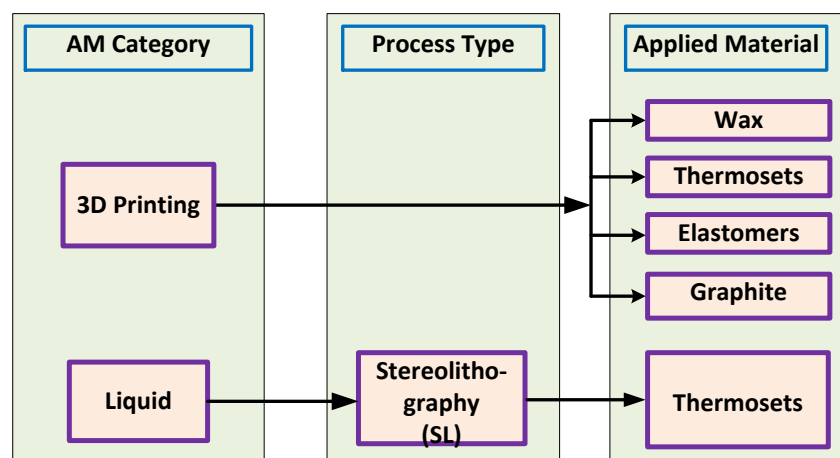


Figure 2.15: Liquid-based AM process^[150]

2.27.2 Powdered-Based Process

The powdered-based processes (Figure 2.16) operate on the principle of consolidating selected portion of powdered material which is sintered using a laser or electron beam to fuse scans of sliced CAD data layer by layer to create the geometry^[139, 152]. After each layer, a re-coater mechanism lays down powder on top of each scanned area, which allows another layer to be built on top of the previous one^[138, 152, 153].

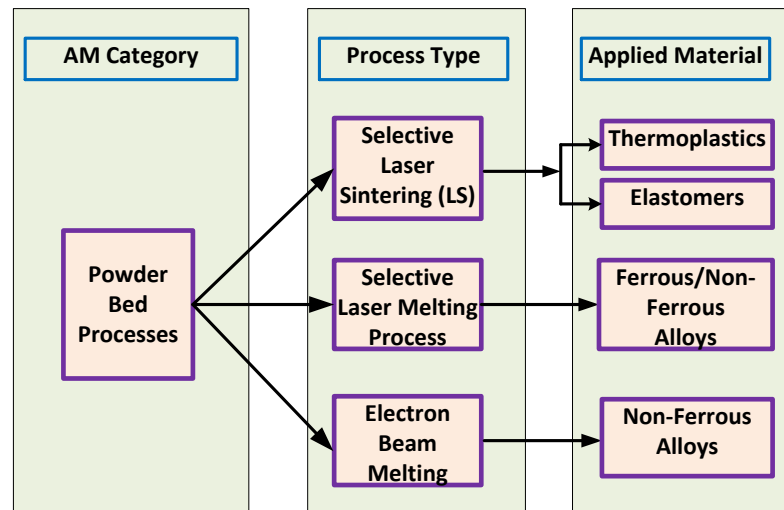


Figure 2.16: Powdered-based AM process^[153]

2.27.3 Material Deposition/Extrusion Process

The deposition processes (outlined in Figure 2.17) work by heating the material using a laser or electron beam source through a nozzle which extrudes it following a path which is pre-defined, depositing a layer on top of a platform, one on top of the other successively to create a three-dimensional geometry^[154, 155].

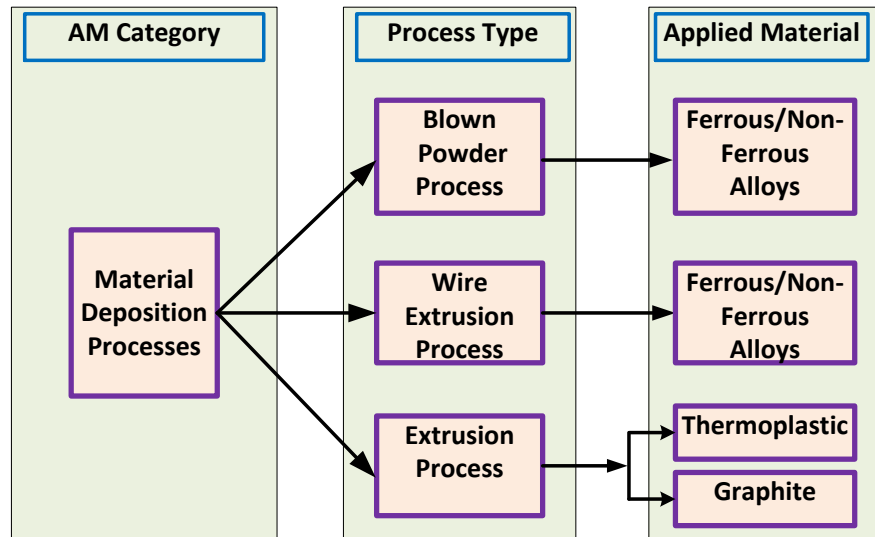


Figure 2.17: Material deposition/extrusion AM process ^[154]

2.28 Environmental Impact of Additive Manufacturing

Conventional manufacturing processes such as casting and moulding produce hazardous industrial waste, therefore, generating a lot of environmental pollutants^[156, 157]; which many countries spend huge amount of money to control^[156, 158]. Additive Manufacturing has emerged as a multidimensional tool used to alleviate these negative environmental impacts^[156, 159]. The constraints imposed on product design by AM are very few compared to the conventional manufacturing processes, as it enables previously separate parts to be combined into a single object with augmented functionality and decreased energy and natural resources required to operate it^[156-159], which will in effect avoid material waste on every sub part, sometimes not recyclable and would therefore have to be thrown to the environment.

2.29 The Competitive Dynamics of 3D Printing

The 3D production ecosystem will have major effects in each of the three major stages of the design-build-deliver model^[160]. It will change the nature of design, increase the interactivity between design and production, and radically localize manufacturing as consumers interact more directly with each other and with manufacturers, some of which act as printer hubs, offering services to anyone with a design to print^[122, 160].

2.30 General Process Comparison

With the many processes of AM technologies in place, it is expedient to combine all strengths and weaknesses, or advantages and disadvantages on one table for fast and easy comparison for the major processes. The Table 2.3 serves as a reference for the selection of a process for specific and appropriate applications^[161] and Table 2.4 compares the additive manufacturing processes to the traditional or conventional manufacturing processes^[146].

Table 2.3: Additive manufacturing process comparison^[161]

Property Name	Stereolithography	Fused Deposition Modeling	Selective Laser Sintering	Direct Metal Laser Sintering	Three Dimensional Printing	Inkjet Printing	Jetted Photopolymer	Laminated Object Manufacturing
Abbreviation	SLA	FDM	SLS	DMLS	3DP	MM, MJM	JP	LOM
Material type	Liquid (Photopolymer)	Solid (Filaments)	Powder (Polymer)	Powder (Metal)	Powder	Liquid	Liquid (Photopolymer)	Solid (Sheets)
Materials	Thermoplastics (Elastomers)	Thermoplastics such as ABS, Polycarbonate, and Polyphenylsulfone; Elastomers	Thermoplastics such as Nylon, Polyamide, and Polystyrene; Elastomers; Composites	Ferrous metals such as Steel alloys, Stainless steel, Tool steel; Non-ferrous metals such as Aluminium, Bronze, Cobalt-chrome, Titanium; Ceramics	Ferrous metals such as Stainless steel; Non-ferrous metals such as Bronze; Elastomers; Composites; Ceramics	Thermoplastics such as Polyester	Thermoplastics such as Acrylic (Elastomers)	Thermoplastics such as PVC; Paper; Composites (Ferrous metals; Non-ferrous metals; Ceramics)
Max part size (mm)	1500 x 750 x 501	915 x 610 x 915	560 x 560 x 762	254 x 254 x 23	1500 x 750 x 702	305 x 153 x 153	491 x 392 x 201	813 x 560 x 508

Min feature size (mm)	0.1016	0.1270	0.1270	0.1270	0.2032	0.1270	0.1524	0.2032
Min layer thickness (mm)	0.0254	0.1270	0.1016	0.0254	0.0508	0.0127	0.0152	0.0508
Tolerance (mm)	±0.1270	±0.1270	±0.2540	±0.2540	±0.1016	±0.0254	±0.0254	±0.1016
Surface finish	Smooth	Rough	Average	Average	Rough	Very Smooth	Smooth	Rough
Build speed	Average	Slow	Fast	Fast	Very Fast	Slow	Fast	Fast
Applications	Form/fit testing, Functional testing, Rapid tooling patterns, Snap fits, Very detailed parts, Presentation models, High heat applications	Form/fit testing, Functional testing, Rapid tooling patterns, Small detailed parts, Presentation models, Patient and food applications, High heat applications	Form/fit testing, Functional testing, Rapid tooling patterns, Less detailed parts, Parts with snap-fits & living hinges, High heat applications	Form/fit testing, Functional testing, Rapid tooling, High heat applications, Medical implants, Aerospace parts	Concept models, Limited functional testing, Architectural & landscape models, Colour industrial design models, Consumer goods & packaging	Form/fit testing, Very detailed parts, Rapid tooling patterns, Jewellery and fine items, Medical devices	Form/fit testing, Very detailed parts, Rapid tooling patterns, Presentation models, Jewellery and fine items	Form/fit testing, Less detailed parts, Rapid tooling patterns

Table 2.4: Contrast between traditional machining and different Additive Manufacturing processes ^[146]

Technique	Acronym	Raw material	Energy consumed	Fixture and tooling	Laser used	Solid residues	Liquid residue	Aerosol residues	Disposal
Machining		Steel, aluminium, alloy	Mechanical energy	Yes	No	Tool scrap, Chips	Fluid mix (cutting, cooling)	Tool particulate, fluid vapour	Landfill, recycling
Stereolithography	SLA	Liquid photopolymer	UV laser beam	No	Yes	Small amount of resin, removed supports	No	No	Incineration, landfill
Selective laser sintering	SLS	Nylon, metal, ceramic, paraffin wax	Higher power laser beam, heat	No	Yes	Material chips,	No	No	Incineration, landfill, recycling
Fused deposition modelling	FDM	Nylon, ABS, ceramic, investment casting wax, alloy	Heat	No	No	Material chips, removed supports	No	No	Incineration, landfill, recycling
Laser engineered net shape	LENS	Metal, binder	Higher power laser beam, heat	No	Yes	Material chips	No	No	Incineration, landfill, recycling
Laminated object manufacturing	LOM	Paper, polymer, metal, ceramic	Higher power laser beam, heat	No	Yes	Material chips	No	No	Incineration, landfill, recycling

Technique	Acronym	Raw material	Energy consumed	Fixture and tooling	Laser used	Solid residues	Liquid residue	Aerosol residues	Disposal
Inkjet printing	IJP	Liquid materials, ink	Piezoelectric nozzle	No	No	Microchips, removed supports	No	No	Incineration, landfill, recycling
Three-dimension printing	3DP	Metal, ceramic, binder	Piezoelectric nozzle, heat	No	No	Removed supports, material chips	No	No	Incineration, landfill, recycling

2.31 Economies of Scale of Additive Manufacturing

Economies of scale are referred to as the bargain in the unit cost of production as the volume of production is increased^[162]. Economies of scale can be the cost reduction due to technological and management factors which can be internal to an organization or cost reduction due to the effect of technology in an industry which is external to an organization^[162, 163].

2.31.1 The End of Economies of Scale of Additive Manufacturing

In economics, a distinction is made between fixed costs (e.g. an assembly line) and variable costs (inputs such as natural resources and labour)^[162]. As volume increases in a conventional manufacturing process, the cost for each unit of output declines since the fixed cost can be spread across more units. This is demonstrated by curve A-B in the Figure 2.18^[163]. The line C-D indicates Additive manufacturing technology where the cost of the first unit will be as expensive or cheap as the thousandth one. This implies that once you own a 3D printer, it can be regarded as a fixed cost, which in this case it is significantly smaller. The unit cost curve for Additive Manufacturing therefore becomes almost a horizontal line, therefore making economies of scale much less important^[163].

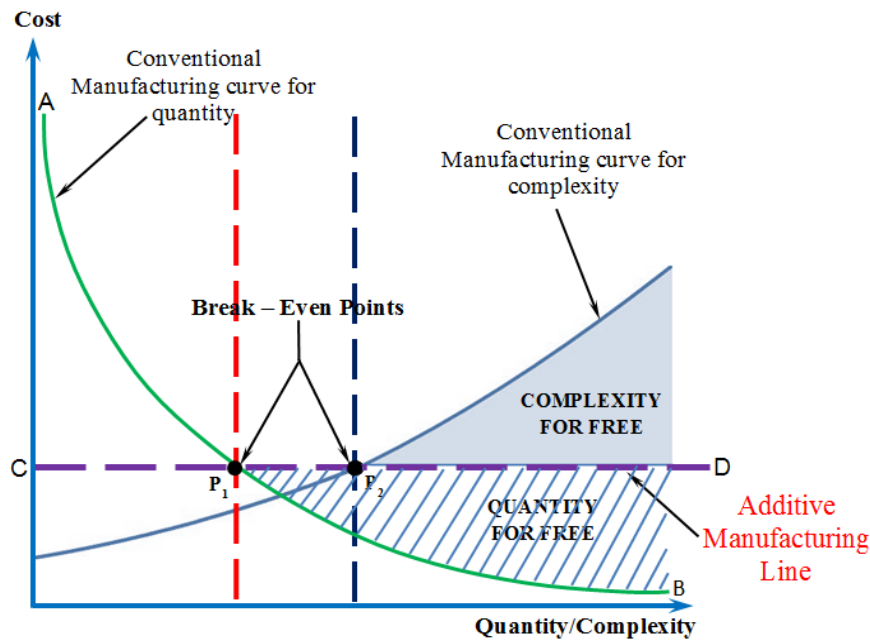


Figure 2.18: Economies of scale of Additive Manufacturing^[163]

2.32 The Inkjet Additive Manufacturing

Even though in the previous section brief description of the AM processes have been dealt with, a detailed description and critical study of the characteristics of the Inkjet process of the AM technology was necessary as the liquid nature of the material considered for this research could be likened to that used for the Inkjet technology. Even though other processes such as SLA^[148] also use liquid, some researchers have used the inkjet process to print PU^[147] but only a single layer and not for specific product, therefore, there is still much to do.

2.32.1 The Inkjet Process Description and Application

The inkjet additive manufacturing process (Figure 2.19) is based on technique of 2D printing which uses a jet to deposit tiny drops of ink onto a paper^[147] or a suitable platform. In the AM process, thermoplastic and wax materials which are held in molten state are used to replace the ink^[164]. The process is usually referred to as thermal phase change inkjet printing because the liquid droplets of ink from the print-head cool instantly and solidify to form a layer of the part. The inkjet process was first commercialised in the 1970's and has since provided a technique for delivering and positioning exact small volumes of liquid at high repetition rates under digital control^[164]. A key feature of all embodiments of this printing method is that it is noncontact^[164]. The process offers the advantages of excellent accuracy and surface finishes^[165]. The limitations of the process include: slow build speeds, few material options, and parts produced are fragile. As a result of the characteristics of the process, it is commonly applied for prototypes used for form fit and fit testing^[165]. Applications of inkjet process may also include jewelry, medical devices, and high-precision products. Inkjet printing devices that use the basic technique described above have been developed by many manufacturers^[166]. Companies such as ObJet, and the Voxel Jet, use a single jet for the build material and another for the support material^[150]. The Multijet Modelling (MJM) of 3D systems implemented into their Thermojet Modeler machines makes it able to use several hundred of nozzles that enables faster build times^[161, 167] and varying part properties.

2.32.2 Principle of Operation

The inkjet process (Figure 2.19) begins with the build material (usually thermoplastic) and support material (usually wax) inside two heated reservoirs in their molten state^[150]. Each of these materials is fed to an inkjet print head which in turn moves in X-Y plane shooting tiny droplets to the required locations forming one layer of the part^[168]. The two materials (build and support materials) rapidly cool and solidify. The completion of a layer is followed by a milling head which moves across to smooth the surface of the layer^[150]. The milling head has a particle collector which vacuums away the particles resulting from the cutting operations. Like any other AM process, the elevator lowers the build platform a height equals the layer thickness (machine resolution) so that the next layer is built. The process is repeated for each layer until the part is complete^[147]. Table 2.5 shows the summary of inkjet printing process.

Table 2.5: Summary of inkjet technology of AM

Abbreviation	MM, MJM
Material type:	Liquid
Materials:	Thermoplastics such as Polyester
Max part size:	304.8 x 152.4 x 152.4 mm
Min feature size:	0.127 mm
Min layer thickness	0.013 mm
Tolerance:	0.025 mm
Surface finish	Very Smooth
Build speed	Slow
Applications	Form/fit testing, Very detailed parts, Rapid tooling patterns, Jewellery and fine items, Medical devices ^[144]

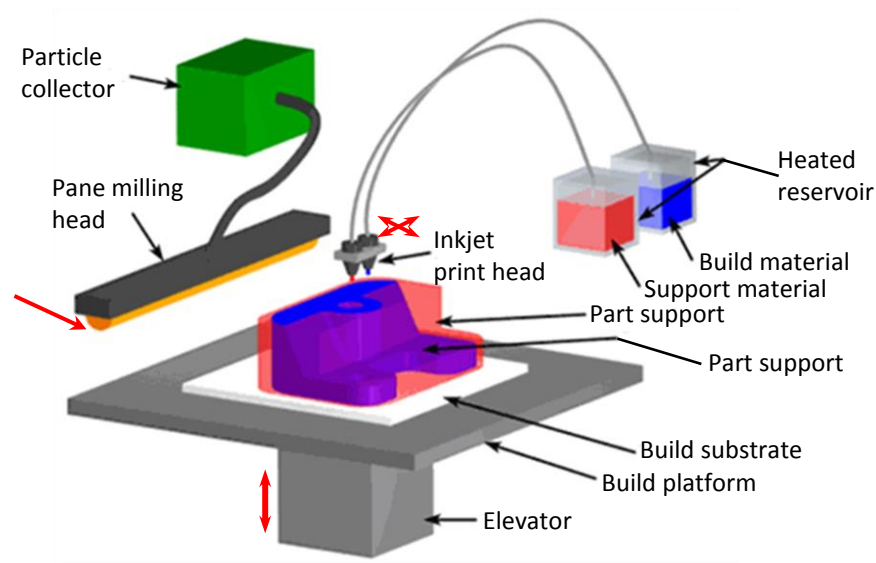


Figure 2.19: Inkjet technology^[147]

2.32.3 Conventional Inkjet Technologies

Any printer that fires extremely small droplets of ink onto a paper or a surface to create an image may be referred to as inkjet printer. Some basic characteristics about the inkjet printers are that: 1) the dots are extremely small (between 10 and 30 dots per millimetre, 2) the dots are positioned precisely, and 3) the dots can have multiple colours for colour printers^[169].

Inkjet technologies are mainly grouped in two, namely: 1) Drop on Demand (DoD), and 2) Continuous Inkjet (CIJ)^[164]. The two techniques use different methods to produce uniformly-sized droplets which are mostly applicable in graphical printing^[170]. The drop on demand mode has liquid droplets produced in response to a digital signal or wave-form^[164]. On the other hand, the CIJ has continuous stream of liquid which is stimulated to break up into drops by the action of a harmonic modulation^[170]. In the CIJ, the modulation frequency and speed of the jet determines the drops separation^[170]. In the most common implementation of CIJ printing, electrostatic charging and deflection are used to select and steer individual drops to define the final printed pattern^[164, 170]. Different actuation methods exist for both DoD and CIJ with the most common ones being; piezoelectric, thermal, and electromagnetic actuators^[164].

2.32.4 Other Methods for Producing Droplets

There are other methods used to produce droplets apart from the common ones mentioned above^[171]. Many of these methods are designed in response to a particular industrial need, such as for the printing of very small droplets, or for colloidal inks that have been used to fabricate three-dimensional periodic structures from colloidal “building blocks”^[171]. Even though the conventional processes are been researched into and developed, different approaches may be studied and developed to better suit some applications as studied by Castrejon-Pita et al^[164]. An example is the generation of very small deposit volumes, the deposition of liquids which contains a high charging of particles, and very high speed printing or the deposition of delicate biological materials^[164]. Some of these technologies are discussed below:

2.32.4.1 Kodak Stream

The Kodak stream technology is an array based, continuous inkjet process which has some significant differences from the CIJ systems that may be advantageous for some applications^[172, 173]. Unlike using the acoustic means to disturb the jets and cause break-up into drops, a small heating element which can be modulated to vary the temperature of the liquid jet at the nozzle is associated with it and also its local surface tension. Surface tension gradients with Maragoni forces are introduced which drives liquid flow away from hot regions thereby controlling the break-up of the jet^[174]. Again, the drops are selected to print by adjusting the timing of the heat pulse such that either small or large drops are created. The small drops are removed by a transverse air flow that is leaving the large drops to be deposited on to the substrate as the drop stream move towards the substrate^[175]. This is as illustrated in Figure 2.20. There are other publications by the Kodak Company describing alternatives to the air flow for selecting drops such as the use of asymmetric heater at the nozzle^[175].

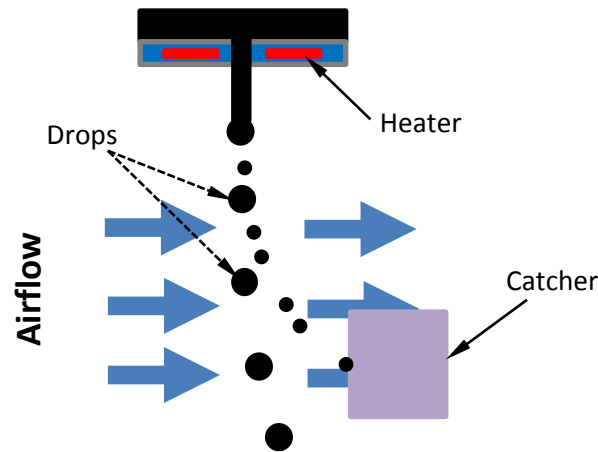


Figure 2.20: Kodak stream technology^[175]

2.32.4.2 Silverbrook

Even though Silverbrook technology employs a variation of the common thermal (vapour bubble) actuation, it stands out from other examples because it possesses certain unique number of features^[176]. The silicon-based microelectromechanical (MEMs) fabrication technique is an example of these, which is used to construct the whole printhead in the form of a stackable chip that enables high nozzle arrays. The print format is usually an array placed across the width of a continuously moving substrate^[176].

2.32.4.3 Electrospray and Tonejet

The electrospray technique is also known as electrostatic or electrohydrodynamic (EHD) printing^[177]. This technique is able to produce small drops from larger nozzles. It has been known for many years and proven by many researchers that an electric field can draw liquid from a nozzle^[178]. The liquid in the nozzle will form a conical shape called a “Taylor cone” under right conditions^[179]. Figure 2.21 illustrates a fine jet or stream of drops drawn from the tip of the cone. Continuous jetting, dripping and, at the highest electrical potential, one or more jets emerging from the nozzle edges are other possible drop-forming modes^[180]. The ability to create very fine jets from larger nozzles is the major advantage of electrospray method^[181]. Notwithstanding the above strength, the modulation of the jet to create ink deposit on demand is a noteworthy challenge^[182].

Castrejon-Pita et al. and Park et al. created a system using small nozzles and a moving table to deposit very small quantities of ink in a controlled way^[164]. In their design, they

were able to use nozzles of internal diameter of $30\ \mu\text{m}$ to produce drops on the substrate with diameters of approximately $8\ \mu\text{m}$. Their tests with nozzles as small as $300\ \text{nm}$ produced spots of diameter approximately $240\ \text{nm}$ ^[164].

With the tone-jet system of the electrospray technique, there are no nozzles but rather there is a cone-like array of pointed electrodes (ejectors) under a liquid with a charged toner particles settled in an inert carrier as isoparaffins^[183]. The charged toner particles are caused to be focused and ejected in a liquid drop by an electric field that are generated between any of the ejectors and an external common electrodes^[183]. The concentration of toner in the bulk liquid is far less than the concentration of toner in the ejected stream. The time for which the field is applied can be used to control the amount of ink ejected so that each pixel will obtain a grey-level capability^[164].

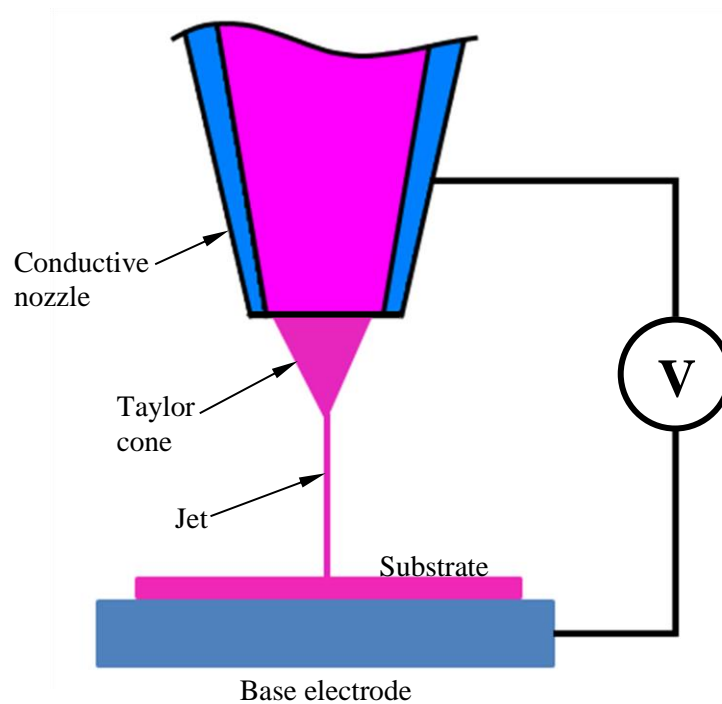


Figure 2.21: Taylor cone and jet^[177]

2.32.4.4 Acoustic Drop Generation

With the acoustic technique, an acoustic energy burst which is focused to a spot on the surface of a liquid which in turn causes a drop to be ejected. One major advantage of this is that no nozzle is required to generate a small drop^[164, 184]. Various methods can be employed for focusing the acoustic energy such as the shaped acoustic and acoustic

Fresnel lenses ^[164, 184]. Figure 2.22 shows acoustic energy from transistor, focused by an acoustic lens on to the surface of a liquid causing a drop to be ejected.

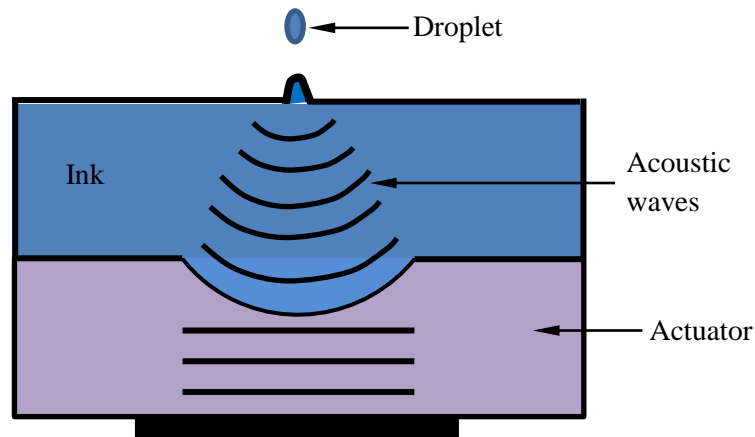


Figure 2.22: Acoustic energy from transistor, focused by an acoustic lens ^[184]

2.32.5 Bubble Jet Print Heads

Powder bed 3D printers mainly use bubble jet print heads. Two primary types of inkjet print head technologies are in use namely: Piezo (Epson printers) and thermal (Cannon and HP printers) ^[185].

2.32.5.1 The Piezoelectric Print Head

In the Epson Micro Piezo print head, microscopic piezoelectric elements (such as crystals and ceramics) are built behind the print nozzles. The application of electric charge on them causes the elements to bend backward, thereby forcing precise amount of ink on the substrate ^[186].

Principle of Operation

Stage 1. During the first stage (Figure 2.23) an electrical pulse is applied to the piezoelectric element behind each nozzle. This causes the element to bend, thereby creating a negative pressure that draws ink from the main ink chamber into the firing chamber ^[186].

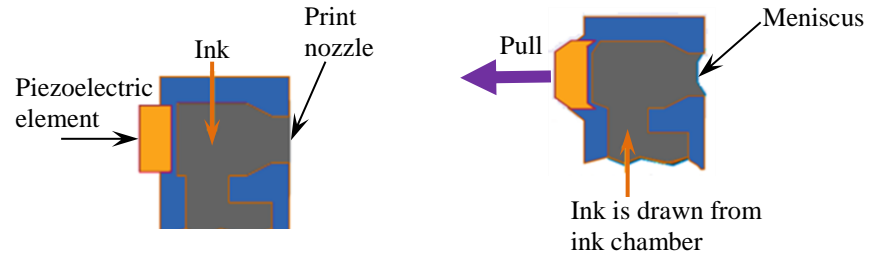


Figure 2.23: Stage 1 of Epson micro print head^[186]

Stage 2.

During the stage 2 (Figure 2.24), electric charge is altered, which causes the piezoelectric element to rapidly push in the opposite direction^[186].

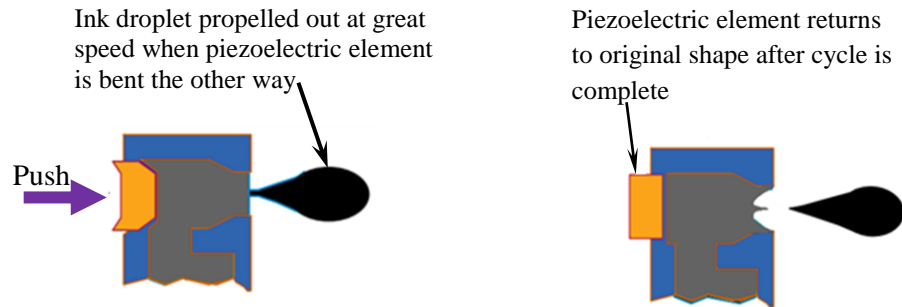


Figure 2.24: Stage 2 of Epson micro print head^[186]

2.32.5.2 The Thermal Print Heads

The thermal inkjet technology as the name suggests, uses heat (as opposed to the piezoelectric type that uses electricity), to force ink from the print head to the substrate. The thermal inkjet technology similar to water bubbles when it boils; works by electrifying microscopic resistors behind the print nozzle. An intense heat is created that vaporises the ink to create a bubble that expands so quickly and the ink literally exploded onto the paper. The chamber cools quickly after the ejection of the ink to allow more ink to re-fill the chamber and repeats the cycle. For a very short time (a period of nanosecond), the ink in the print head is close to 106°C^[186].

Principles of Operation

Three stages are involved in the principle of operation of the thermal inkjet print head.

Stage A

At the first stage, the ink in the firing chamber is rapidly heated by a resistor until it boils and therefore begins to form an air bubble (Figure 2.25 ‘A’).

Stage B

At the second stage, the air bubble in a microsecond grows until it explodes the ink out through the nozzle and onto the medium (Figure 2.25 ‘B’).

Stage C

After the ink is propelled out, the bubble cools, contracts, and collapses. More ink is drawn in from the main ink chambers by the resulting vacuum to repeat the cycle (Figure 2.25 ‘C’).

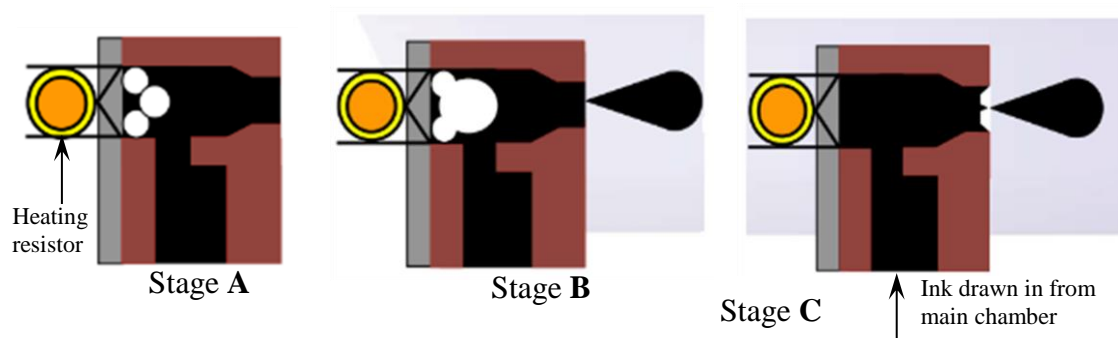


Figure 2.25: Principles of operation of thermal inkjet print ^[186]

2.32.6 Comparison of the Piezoelectric and the Thermal print heads

Each of the above print head has some advantages and disadvantages. The Micro Piezo print head provides a sharper, grain-free print, with smoother tonal transition because of its more precise control, and is able to vary droplet sizes^[186]. Table 2.6 compares and contrasts the Piezoelectric and the Thermal print heads^[187].

Table 2.6: Comparison of Epson Micro Piezo and Thermal system ^[187]

	Epson Micro Piezo System	Thermal System
Ink Ejection Method	Ink ejected by mechanical pressure exerted by piezoelectric element.	Ink ejected by creating and exploding an air bubble by rapidly heating the ink.
Performance	Ink drop volume controlled by voltage for precise and variable droplet size and high speed ejection.	Achieves higher speeds by increasing nozzle count.
Resolution	Epson Micro Piezo print heads allow for precisely sized drops of ink of up to five different sizes to be ejected onto the medium, resulting in sharper, grain-free prints with smoother tonal transitions.	Thermal inkjet printers cannot control ink droplet size for individual nozzles.
Ink Compatibility	The low temperature operation of Epson Micro Piezo print heads make them compatible with a wide range of inks, including dye and pigment types, solvent inks, and ultraviolet cure inks.	Limited ink options due to extreme heat involved. Volatile inks are impossible for use in the high heat operation of conventional thermal inkjet printers.
Durability	Epson Micro Piezo print heads run much cooler than thermal inkjet ones and can provide reliable operation for the life span of the printer. Therefore, no Epson ink cartridge needs a print head attached, making them more affordable, and environmentally friendly.	Most printers with thermal inkjet print heads need them to be changed regularly because of the extreme heat involved in their operation that will damage them with prolonged use. Therefore, expensive new print heads are usually built into ink cartridges and are replaced with every cartridge change.
Power Consumption	Epson Micro Piezo print heads use less power than thermal inkjet print heads because the piezoelectric method of ink ejection is far more efficient.	The resistors used by thermal print heads to heat the ink consume a much higher amount of power compared to the piezoelectric method.

2.33 A Review of Reactive Inkjet Printing of Polyurethane

Reactive inkjet printing which is one of the Additive Manufacturing technologies was used to create micron-scale polyurethane structures, such as dots, lines and pyramids by Krober et al. and published in 2009^[26]. The structures were fabricated *in-situ* using inkjet printer to print the two resins (polyol and diisocyanate) successively from two separate print heads. According to the research, the time taken for the structures to cure was within five minutes. Even though this was a remarkably fast foaming and curing time, it could further be improved. Various AM techniques such as stereolithography^[5], fused deposition modelling^[188], selective laser sintering and 3D powder bed printing^[189] were the few that were mentioned. Nonetheless, it would have been an addition if a brief description of the given examples were mentioned.

AM technologies have some drawbacks and one of the main ones being that they have limited range of materials that could be processed directly^[5]. Examples are bio-ceramics, biodegradable polymers, and silicones which are accessible only by post-treatment processes^[190]. As such, many researchers are researching into the discovery of new materials and improving of the AM machines to expand its material application. Hence, this research works to expand the material characterisation of AM by looking at other possible and more effective way of dispensing polyurethane foam for medical scaffolds.

According to the paper many of the AM processes such as fused deposition modelling, 3D printing, or stereolithography have practically been used direct printing purposes.^[148] Currently, SLS is been used to print metallic end use parts such as for aircraft parts^[95]. Inkjet has been used in wide range of application beyond its initial purpose of dispensing ink for the printing of office documents by the inkjet being dosed with different kinds of materials like conductive polymers and nanoparticles^[26].

The potential of PU on Additive Manufacturing has been studied by Piccin et al.^[191]. In their study, they produced capillary electrophoresis microchips from the material in less than one hour^[191], using photolithography as the method for micro-patterning^[26]. To achieve the multi-micron feature resolution typically associated with AM techniques, an inkjet process was considered as a synthesis tool which is a precise method for building up small structures using some reactive materials^[26]. Krober et al. records that the multi-micron feature resolution typically associated with AM were achieved using inkjet

printing process. They demonstrated that defined micron-scale PU-based structures could be fabricated via reactive inkjet printing starting from the corresponding monomers in a reactive, *in-situ* manner on glass substrate. The approach yielded unique, cross-linked thermoset PU materials with spatial resolution in the range of tens of microns^[26]. In exploring the use of inkjet printing as a technique for undertaking moisture-sensitive chemical reaction, they considered the process as being used to demonstrate a successful technique for material handling involved in some diverse fields such as free-polymerisation^[51], deoxyribonucleic acid (DNA) synthesis and peptide synthesis^[192].

As stated, earlier in the literature, the chemistry of PU involves the mixing of two separate inks (diisocyanate and Polyol) and other additives. In this case the two inks were printed in successive layers on a surface, and allowed to react to form a urethane bond^[26]. The addition of cross linking agent (trimethylolpropane) was to ensure solvent-resistant, thermostat film with micro-scale structural detail. In their quest to select the appropriate diol, hydroxyl-terminated telechelic poly (ethelyne glycol) (PEG), and hydroxyl-terminated telechelic poly (propylene glycol) (PPG) which have been well-studied were chosen respectively^[26]. Their aim was to determine the effect that the role of a side chain had on the quality of the final film. To obtain a low viscosity as a printable material, a lower mass with a molar mass of 400 mPa's at room temperature according to the vendor's report was used. The aprotic, polar solvent *N,N*-dimethylformamide (DMF) was added to further reduce the viscosities into more manageable range, thus giving inks that were easily printable^[26]. The diisocyanates selected for the second set of inks were isophorone diisocyanate (IPDI) and 2,4-toulene diisocyanate respectively^[26]. These were made printable by adding small aliquot of DMF, and also, a catalyst bismuth neodecanoate (BiNeo) was added to promote the reaction^[26]. The key factors of AM including how subsequent layers of materials behave when they are deposited on previously deposited ones, feature sizes, surface spreading with the simple geometry possible were considered^[26]. In order to examine these properties more readily, substrates were spin-coated with the appropriate PU solution preceding the printing^[26].

A literature of well-developed approach to the studying of polymerization kinetics in cross-linked urethane films developed by Fourier transform infrared spectroscopy (FT-IR) spectroscopy was monitored for the progress of the reaction *in-situ*^[193, 194]. The materials used for the experiment are illustrated in Table 2.7.

Table 2.7: Comparison of inks for reactive inkjet printing^[26]

<i>PPG-Ink</i>			<i>IPDI-Ink</i>		
Polyol	Cross-linker	Solvent	Diisocyanate	Catalyst	Solvent
poly(propylene glycol) (PPG)-400/ μL	Trimethylolpropane (TMP)/g	Dimethylformamide DMF/ μL	Isophorone diisocyanate (IPDI)/ μL	Bismuth neodecanoate (BiNeo) (wt%)	Dimethylformamide DMF/ μL
2000 (5 mmol)	0.59 (5.6 mmol)	1792	2834 (1.35 mmol)	0.46	958

2.33.1 Surface Preparation for Substrates

Available glass microscope slides with dimensions 75 mm x 25 mm supplied by Marienfeld, Lauda-Königshofen, Germany, were subsequently washed with soapy water, acetone, and lastly ethanol^[195]. There was a final rinsing of the glass slides using isopropanol after which the slides were dried under laminar flow of air. The glass substrate coated with a thin PU film was prepared by spin-coating^[26]. Equal amounts of the *PPG-Ink* and the *IPDI-Ink* was prepared by pre-mixing and subsequently placing it onto the glass substrate for the spin-coating of the PU. This was followed by heating the glass substrate to 90°C for 10 min^[26].

2.33.2 Inkjet Printing

Krober et al. performed inkjet printing using an Autodrop system which is piezoelectric-driven (Microdrop Technologies, Norderstedt, Germany)^[26]. Two 100 μm print heads which could be moved in vertical (z) direction was attached to the system. Droplets of both inks were generated using 158 to 160V, pulse width of 38 to 40 μs , with a fixed frequency of 200 Hz. A fiducial camera, illuminated by a stroboscope light source was used to follow droplet formation^[26]. In-house programmed macros was used to carry out printing with ten sets of five parallel lines printed by increasing the dot spacing in steps by 10 μm from 40 to 100 μm ^[26]. The finest dot spacing was originated to be 70 μm for the *PPG-Ink*, and 80 μm for the *IPDI-Ink*. The two print heads were calibrated and spatially synchronised with each other prior to use to ensure accuracy and reproducibility with the heating plate that holds the glass substrate set to a temperature of 90°C^[26].

Krober discussed that even though inkjet printing may be used to dispense a wide range of materials, there are some physical limitations to practical applications. The solutions

(inks) to be printed must meet certain acceptance criteria based on physical parameters such as viscosity, vapor pressure and surface tension^[26].

If the viscosity is too high, the ink cannot be ejected from the nozzle, and will therefore not be a printable material. Similarly, if either the surface tension or the vapor pressure is too low, stable droplet formation becomes difficult to achieve. The solvent used was DMF, as that demonstrated good printability, and suitable drying properties^[26]. Two separate inks, the first containing poly (propylene glycol) 400 dissolved in DMF, and the second based on isophorone diisocyanate were subsequently inkjet print onto each other on the substrate. With the introduction of the cross-linking agents, the reactants after printing cured and hardened very fast^[26].

Even though industrial polyurethanes are produced by continuously stirring the base materials to be homogeneous, Krober down-scaled the reaction by bringing the reagents together as sub-nanolitre droplets to act as wall-less microreactors. They further demonstrated that effective mixing could be achieved without any additional mechanical aid^[26]. The mixing behaviour of two components was followed by adding a fluorescent dye to *PPG-Ink*. Afterwards, confocal laser scanning microscopy was used to observe the impact of a droplet of the *IPDI-Ink* into a droplet of *PPG-Ink*. The results obtained from the fluorescence images show that no concentration gradient within the droplets, indicating homogeneous mixing of the two components within the droplets occurs^[26].

In summary, Krober et al have demonstrated that micron-sized PU structures can be fabricated by reactive inkjet printing^[26]. In their technique, two separate nozzles each containing monomers IPDI and PPG were used based on the techniques of inkjet printing of droplets of two inks. The droplets of the ink were made to merge on the substrate and polymerise *in-situ* to form PU structure in a period of three minutes^[26]. This research will therefore address some of the critical issues such as, the viscosity and other flow characteristics in its design for the proof of concept.

CHAPTER THREE

CHARACTERISTICS OF POLYURETHANE FOAM

3.1 Introduction

Polyurethane foams are produced by chemical reaction between two base components (polyol and isocyanate) in the form of liquid and a blowing agent of low boiling point such as carbon dioxide or pentane to vary its properties. The base materials react directly upon mixing thereby building a polymer matrix (polyurethane). Other ingredients are usually added to modify its properties, which in turn widen its scope of applications. The ingredients considered for this research are the two main constituents of PU (i.e. polyol and diisocyanate).

3.2 Testing Methodology and Equipment

3.2.1 Screening Tests – Visual Assessment or Inspection

Initial screening tests were conducted to reveal the key mechanical property attributes and/or inadequacies in the material system candidates. It was also to narrow the number of tests by selecting the reasonable and logical parameters for further experiments and analysis.

The mixing ratios considered for the screening tests were as illustrated in Table 3.1. The 50:50 mixing ratio (representing 50% of Part A and 50% of Part B) with a total volume of 50 ml was used as the reference as many researchers have used that with varying additives to suit their requirements. Part A was increased to 70% and Part B decreased to 30%, both at intervals of 5% and part A decreased to 30%, with part B increased to 70%, also at intervals of 5%. Therefore, the total mixing ratio considered for the screening test was 9.

Table 3.1: Comparison of inks for reactive inkjet printing

Part A (%)	70	65	60	55	50	45	40	35	30
Part B (%)	30	35	40	45	50	55	60	65	70

3.2.1.1 Screening Tests Results – Visual Analysis

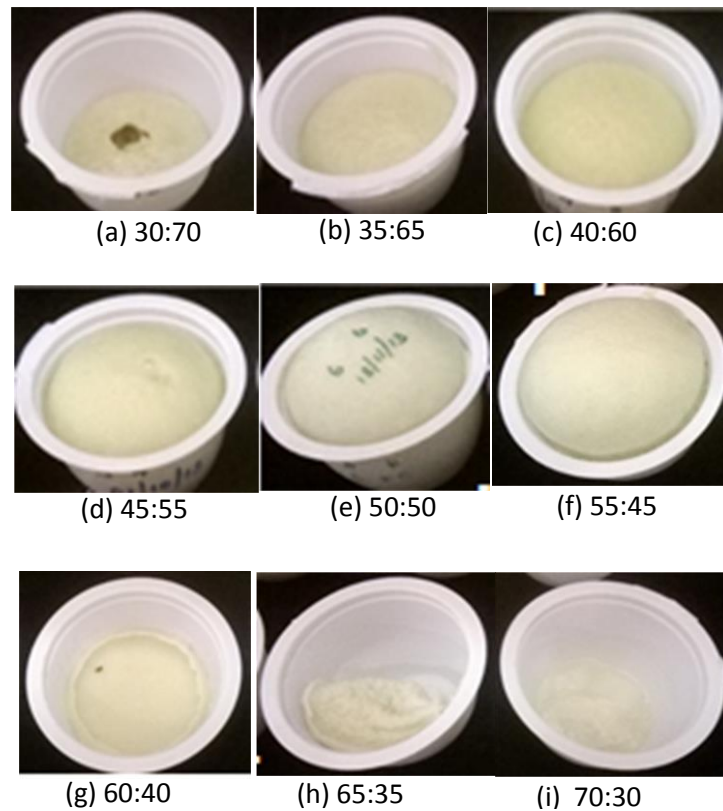


Figure 3.1: Foam blocks obtained from screening tests

Results obtained (Figure 3.1) indicated that for mixing ratios of 60:40, 65:35 and 70:30 (Part A higher than 55%), the foam produced was soft and dimensionally unstable and worsened with further increasing of part 'A'. In the other direction of the mixing ratio where part A decreased whilst part B increased (i.e. 45:55, 40:60, 35:65, and 30:70), a rise in the foam strength was obtained. However, above 60% of part B, the foam produced was very brittle, and could be crushed by hand force. It was therefore agreed to use only 40:60, 45:55, 50:50 and 55:45 mixing ratios for further investigations and analysis.

3.2.2 Comparison of Foam Volumes at Different Mixing Ratios

Four moulds of the same internal dimensions, 90 mm x 90 mm x 220 mm (Figure 3.2) were used to be able to cut out a complete sample size with each containing one mixing ratio at the same temperature (room temperature of 20°C). The mixing ratios considered were 40:60, 45:55, 50:50, and 55:45. Each of these represented a total volume of 100ml. For example, 40:60 mixing ratio indicated 40 ml of part A (polyol) and 60ml of part B (diisocyanate). The volume of foam blocks obtained was compared.

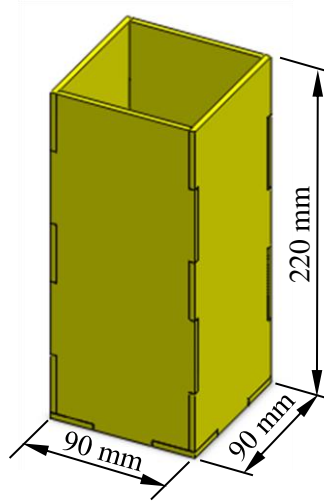


Figure 3.2: Mould for foam volume comparison

3.2.3 Measurement of Densities of Different Mixing Ratios PU Foam

Moulds of internal dimensions 192 mm x 192 mm x 192 mm (Figure 3.3 'a') were prepared and used to cast foams of different mixing ratios; 40:60, 45:55, 50:50, and 55:45 at pre-heat temperature of 20°C. The outer skins of the foam blocks produced were removed to a depth of 10 mm to ensure that test specimens are cut from homogeneous materials. The direction of foaming was taken into consideration (Figure 3.3 'b') to compare the characteristics of the material in adjacent directions.

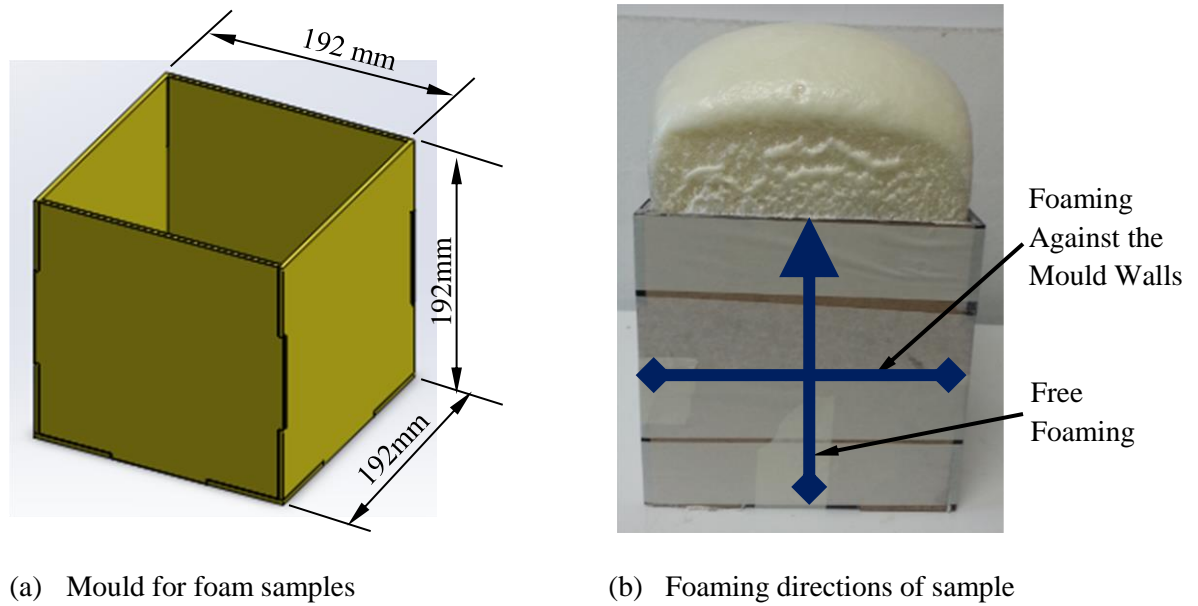


Figure 3.3: Mould and foaming direction of foam sample

Foam dimensions of 170 mm x 170 mm x 170 mm were cut from the blocks using the CNC machine and weighed using a calibrated scale (Figure 3.4) of readability and reproducibility of 0.001 g and ± 0.003 g linearity, 3 seconds stabilization and standard error of $\pm 0.5\%$.

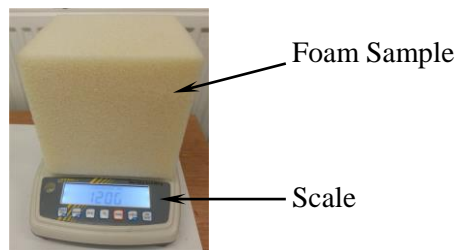


Figure 3.4: Sensitive scale for weighing foam block

3.2.4 Measurement of Porosity of Different Mixing Ratios

The porosities of foams produced were determined using the liquid displacement method in Figure 3.5 to agree with the measurement of the densities to satisfy their already proofed relationship that density is inversely proportional to porosity. In this method ethanol which penetrates into the pores of foam was used as the displacement liquid. A

specimen (Figure 3.6) of each of the PU foam scaffolds produced was dried at room temperature and placed in a graduated cylinder which is filled with ethanol to an initial volume (V_1) and subjected under vacuum for 20 minutes for the ethanol to fill the pores of the scaffold. The volume (V_2) of the ethanol with the scaffold was noted^[29]. The scaffold was then removed from the ethanol and the remaining volume (V_3) was noted^[29]. The percentage porosity (P (%)) of the scaffold was then calculated as follows:

$$P (\%) = \frac{(V_1 - V_3)}{(V_2 - V_3)} \times 100 \quad \text{Eqn. (3.1)}$$

Where; ($V_2 - V_3$) = total volume of the scaffold,

And; ($V_1 - V_3$) = volume of ethanol retained in the scaffold sample.

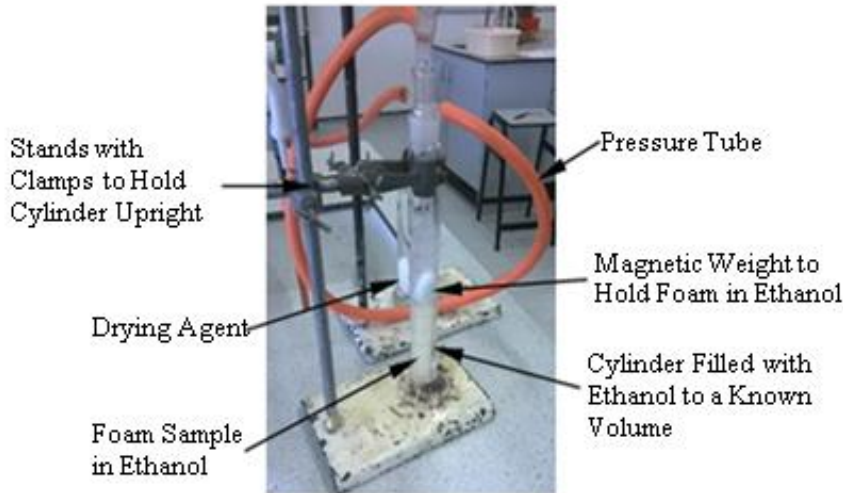


Figure 3.5 Liquid displacement vacuum set-up for porosity measurement



Figure 3.6: Foam specimens for porosity measurement

3.2.5 Comparisons of Scaffold Structures at Different Mixing Ratios

Samples of the foams produced at 20°C with mixing ratios of 40:60, 45:55; 50:50, 55:45 were scanned using an FEI Quanta 200 Scanning Electron Microscope (SEM)

(Figure 3.7)^[196] coupled with Energy Dispersive X-ray analysis (EDX) at 2 mm working distance in order to assess the structure of these samples. The scanning was done in both free foaming and restricted foaming (x and y respectively) directions. For fair comparison, the samples were cut to the same size and height and placed on the SEM turntable which has the capacity to carry seven different samples at the same time and at the same magnification.



Figure 3.7: FEI Quanta 200 FEG^[193]

3.2.6 Tensile Strength Testing

Standard tensile specimen sizes (Figure 3.8) were cut from the foams of different mixing ratios according to ASTM D3039 (Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials) in both free foaming direction and restricted foaming direction. Three specimens each were then tested using the Instron E3000 (Figure 3.9) with a 3 kN Load cell under a crosshead speed of 8 mm/min and $\pm 0.005\%$ load cell capacity.

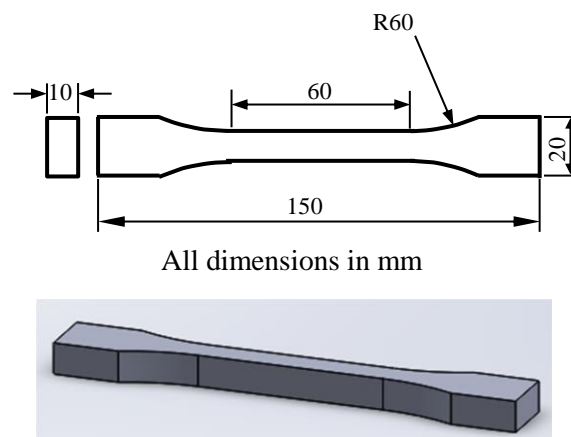


Figure 3.8: Standard tensile test specimen

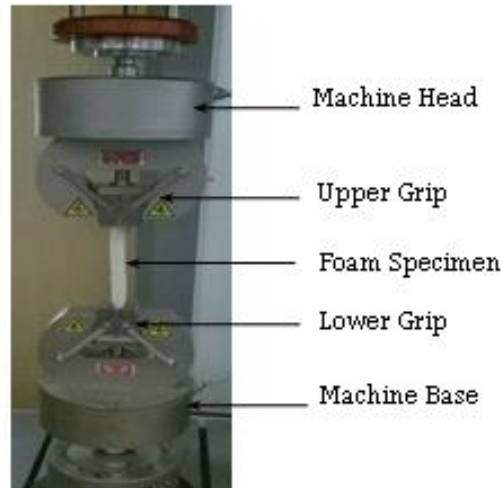


Figure 3.9: Tensile testing using Instron–E-3000

3.2.7 Compressive Strength Testing

For compression testing, blocks were cut to known measurements of (40 mm x 40 mm x 40 mm) in both free and restricted foaming (x and y) directions according to ASTM 3410 M standard (standard test method for compressive properties of polymer matrix composite materials) as shown in Figure 3.10. The specimens were then tested using the Instron–3382 (Figure 3.11) with a 100 kN Load cell under a crosshead speed of 8 mm/min $\pm 0.2\%$, maximum resolution of 0.1 N and a load measurement of $\pm 0.5\%$.

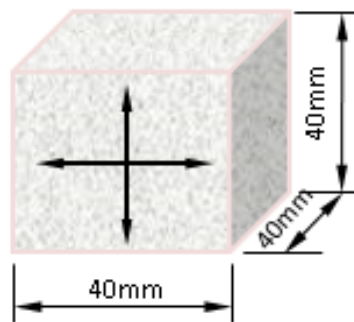


Figure 3.10: Block sample for compressive test

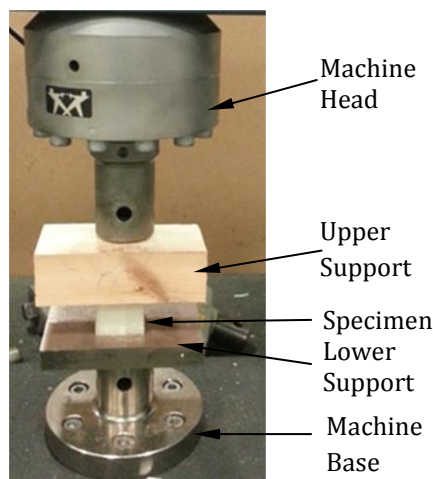


Figure 3.11: Compressive test using Instron-3382

3.2.8 Effect of Pre-Heat Temperature

The 50:50 mixing ratio was maintained and the main constituents (polyol and diisocyanate) were pre-heated from 20°C to 100°C at intervals of 10°C in a graduated clear glass container to view the reaction at parallel. The time taken for each mixing ratio to complete foaming from the beginning of bubbling (nucleation) to complete foam rising (cure) was recorded using a stop clock. The processes mentioned above (section 3.2.3–section 3.2.7) were repeated to determine the densities, porosities, tensile strengths, and compressive strengths of the pre-heated foams.

3.2.9 Measurement of Viscosities of the PU Resins

The viscosity of fluid is defined as the measure of the fluid's resistance to gradual deformation by tensile or shears stress. For liquids, viscosity could be described by the rate at which it flows. The phenomenon is measured with various types of viscometers and rheometers. Viscosity is usually measured in centipoise (cP).

Where, $1 \text{ cP} = 0.001 \text{ N.s/m}^2 = 1 \text{ mPa.s}$.

As one of the basic requirements of a fluid to be printable, its viscosity has to be low. Again, as this research will look at the PU resins being dispensed through nozzles of small diameters, therefore, the need to study the variation of the viscosities of the resins at different temperatures.

The Viscolite 700HP Bench Viscometer (Figure 3.12)^[197] which is a hand-held or bench mounted instrument was used to measure the viscosities of the resins. It can be used with any volume of fluid. This is different from the conventional rotating cylinder viscometers as there is no specific quantity of fluid, or size of vessel, required for its accuracy^[197]. The instrument has a calibrated range from 0 to 5,000 cP, temperature range of -40°C to $+150^{\circ}\text{C}$, and transformer/adaptor of 12 V 800 mA^[197]. When the fluid level is below 'B' (i.e. $>35 < 62$ mm) (Figure 3.12), the instrument measures only viscosity but when the fluid level is above 'B' (i.e. > 62 mm), it measures both viscosity and temperature^[197].

3.2.9.1 Principle of Operation of the Viscolite 700HP Viscometer

The sensor element consists of a shaft with an end mass, or bob, which is made to vibrate (also called resonate) at its natural frequency. When vibrating, the moving parts of the sensor shear through the fluid. As this shearing takes place, energy is lost to the drag forces on the sensor caused by the viscosity of the fluid. The loss of energy in each cycle of vibration is measured by the sensor electronics and the microprocessor in the display unit. From this energy loss, the actual viscosity of the fluid is determined^[197].

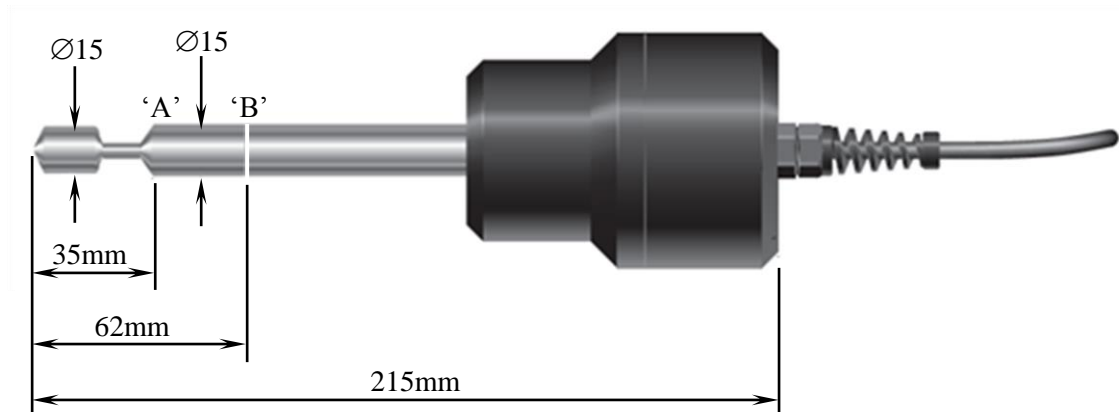


Figure 3.12: Viscolite 700 Viscometer probe^[194]

A measuring beaker was filled with part 'A' resin (polyol) to a level that will leave enough allowance between the tip of the viscometer probe and the internal base of the container, and above the 'B' reference line to ensure that both viscosity and temperature are measured at the same time. With the instrument probe clamped and let in the resin, the first measurement of the viscosity and temperature were taken without heating.

The resin was heated to a temperature of 35°C using Carbolite oven and the viscometer probe let in the heated resin and allowed the instrument to read 30°C and the viscosity taken simultaneously. This was repeated for 40°C at 45°C; 50°C at 55°C; 60°C at 65°C; 70°C at 75°C; 80°C at 85°C; 90°C at 95°C; and 100°C at 105°C. The entire set-up is as shown in Figure 3.13.

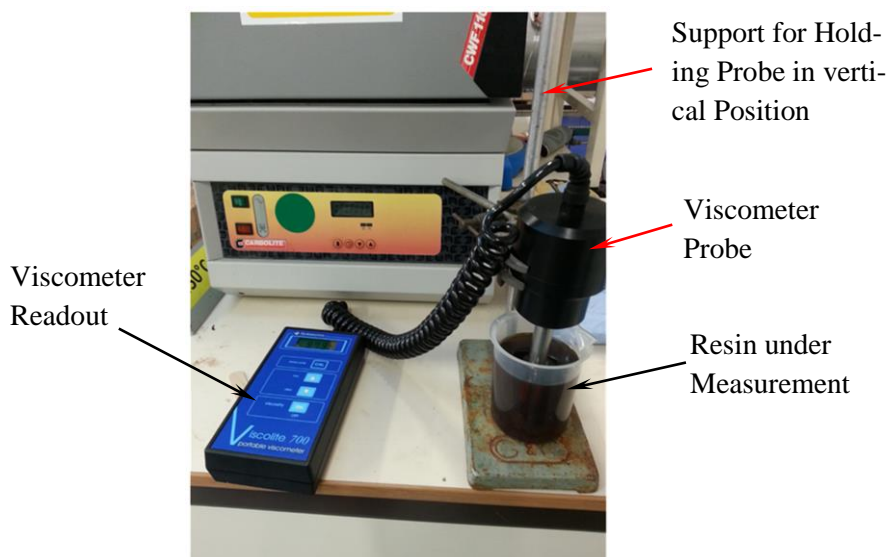


Figure 3.13: Viscolite 700 viscosity measurement set-up

The process was repeated for part 'B' resin (diisocyanate) and the results recorded. The entire experiment was repeated three times and average taken for analysis.

3.3 Results and Discussion

3.3.1 Volume Comparison of Varying Mixing Ratios

The results obtained in foaming a total volume of 100ml of polyol and diisocyanate at mixing ratios of 40:60, 45:55, 50:50, and 55:45 at 20°C is outlined in Figure 3.14. In comparing the obtained blocks, it was observed that the volume of the foam increases with the same initial total volume of resins with increasing percentage volume of polyol. From the diagram, it is clearly seen that the volume of foam made from 40:60 mixing ratio is less in volume than 45:55 mixing ratio; the volume of 45:55 mixing ratio being less than 50:50 mixing; and the 50:50 mixing ratio being less than the 55:45 mixing ratio. It could therefore be concluded that, for a fixed volume of PU resins (50:50

ratio of part A and part B respectively), the volume of foam produced increases with increasing part A.

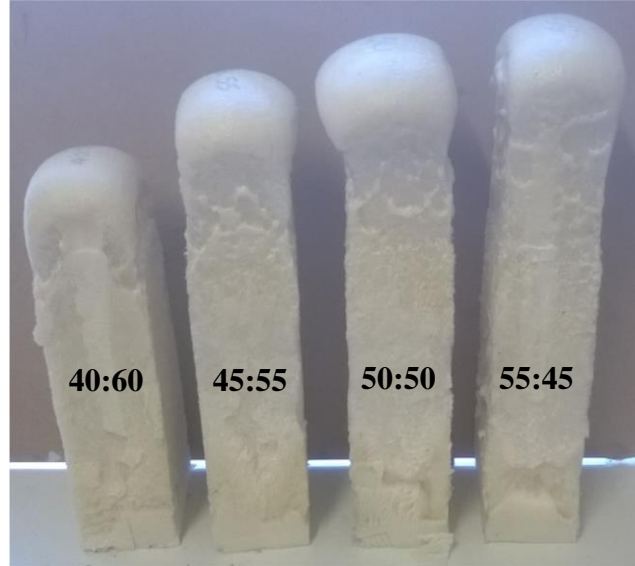


Figure 3.14: Foam blocks at different mixing ratios

3.3.2 Density Test Results

3.3.2.1 Densities of Different Mixing Ratios

The densities for the produced foam using different mixing ratios are illustrated in Table 3.2. The average density for the 55:45 mixing ratio was 46.3 kg/m^3 , and that obtained from 50:50 mixing ratio was 48 kg/m^3 , whilst that obtained for 45:55 mixing ratio was 53.3 kg/m^3 . The average density obtained from the 55:45 mixing ratio indicates a 3.8% reduction when compared to the density of the 50:50 mixing ratio whilst that obtained for the 45:55 mixing ratio indicates an 11% increase when compared to the result for the 50:50 mixing ratio.

From Figure 3.15, it could be realised that the density of the PU foam increases with increasing part B (diisocyanate) of the PU main constituents and vice versa.

Table 3.2: Densities of varying mixing ratios

Mixing Ratio	Density (kg/m ³)				Uncertainty	STDEV
	1	2	3	Mean		
55:45	46.3	46.1	46.2	46.2	0.1	0.10
50:50	48.3	47.5	48.2	48.0	0.4	0.44
45:55	53.0	52.9	54.0	53.3	0.6	0.61
40:60	61.9	61.6	61.9	61.8	0.1	0.17

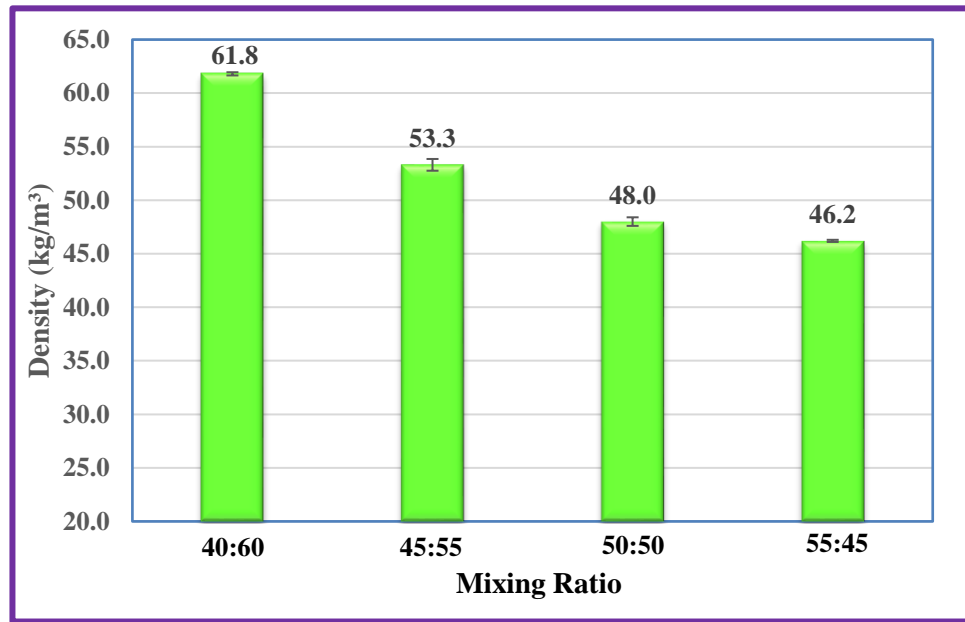


Figure 3.15: Mixing ratios versus densities

Figure 3.15 shows the relationship between the mixing ratio variation and density of PU foam.

3.3.2.2 Densities of Varying Pre-Heat Temperatures – 50:50 Mixing Ratio

The results obtained by maintaining the mixing ratio at 50:50 and pre-heated from 20°C to 100°C at varying interval of 10°C show that the density decreases with increasing pre-heat temperature up to 60°C and increases with increasing pre-heat temperature beyond 60°C up to 100°C, as shown in Table 3.3 and Figure 3.16.

Table 3.3: Densities of varying pre-heat temperature

Pre-Heat Temp	Density (kg/m ³)					Range	STDEV
	1	2	3	Mean	% Decrease with Ref. to Room Temp (20°C)		
20	48.1	47.8	48.2	48.0	-	1.0	1.00
30	44.6	44.8	44.5	44.6	7.8	1.1	1.08
40	43.5	43.0	43.6	43.4	10.7	0.1	0.17
50	43.1	43.0	42.9	43.0	11.7	0.2	0.17
60	42.4	42.5	42.8	42.6	12.5	0.2	0.17
70	43.0	43.2	43.1	43.1	11.2	0.3	0.31
80	43.6	44.1	43.2	43.6	9.9	0.1	0.17
90	44.4	44.6	44.2	44.4	7.5	0.3	0.36
100	45.4	45.1	45.7	45.4	5.4	0.3	0.30

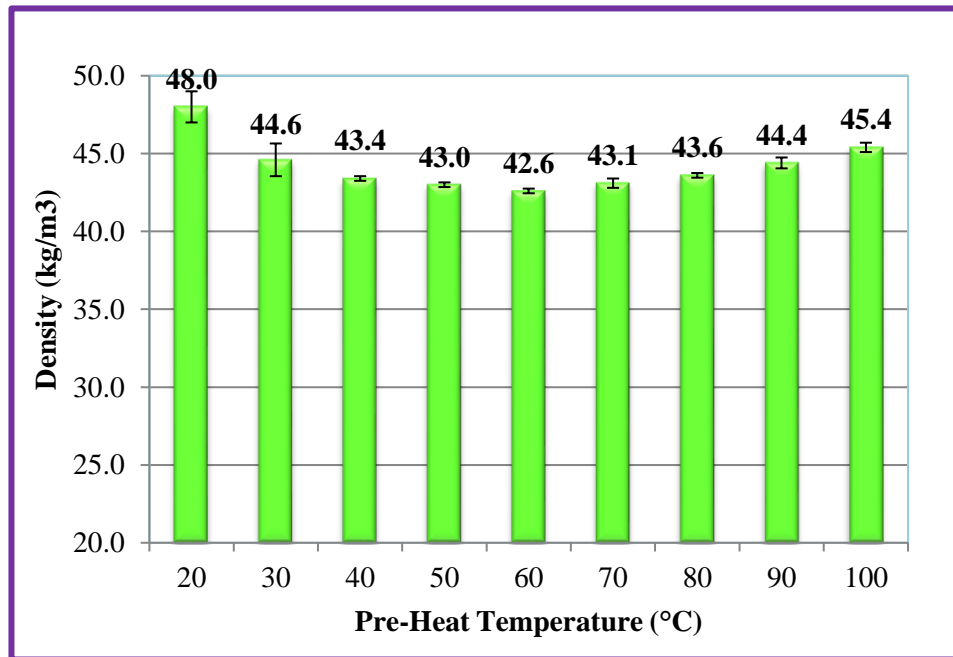


Figure 3.16: Pre-heat temperatures versus densities

Figure 3.16 shows the relationship between the varying pre-heat temperature from (20°C to 100°C) and density of PU foam.

3.3.3 Porosity Test Results

3.3.3.1 Porosities of Varying Mixing Ratio

Porosities for the produced foam using different mixing ratios are illustrated in Table 3.4. From the results obtained using the liquid displacement method, it could be observed that the 55:45 mixing ratio had the highest porosity of 43%. This was followed by the 50:50 mixing ratio with a porosity of 33%, the 45:55 mixing ratio having 29%, and the porosity of the 40:60 mixing ratio being the least at 26.5% as plotted in Figure 3.17. These can be controlled precisely by adding other chemicals to obtain the required standard of foam for the desired properties. The porosity of the 55:45 mixing ratio compared to that of the 50:50 mixing ratio indicates an increase of 30%. The 45:55 mixing ratio indicates a 12.1% decrease and that of the 40:60 indicates a 12.1% reduction.

Table 3.4: Porosities of varying mixing ratios

Mixing Ratio	Porosity (%)					
	1	2	3	Mean	STDEV	Range
55:45	42.5	44.0	43.0	43.2	0.8	0.8
50:50	31.9	32.8	34.3	33.0	1.2	1.2
45:55	30.0	27.5	29.5	29.5	1.3	1.3
40:60	27.0	28.0	26.0	27.0	0.3	1.0

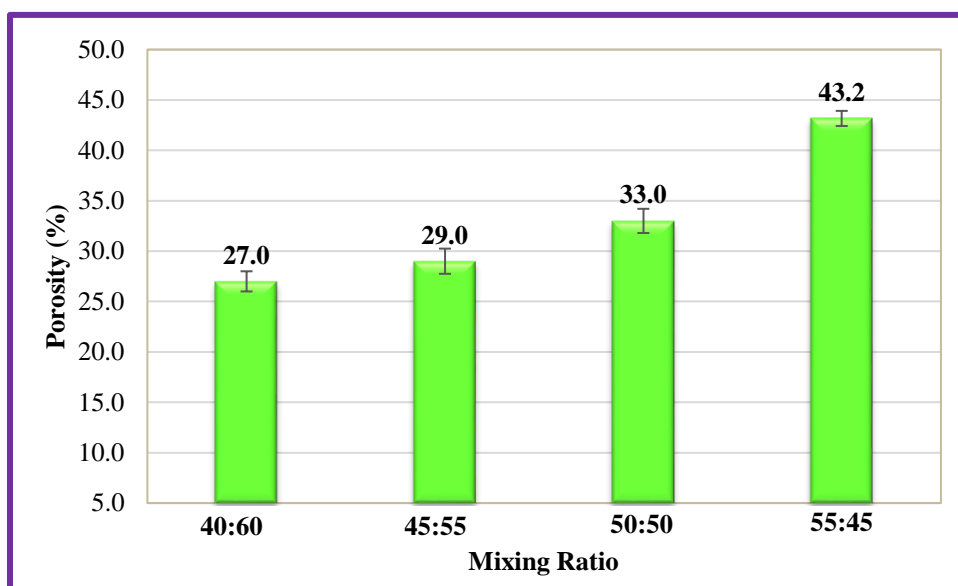


Figure 3.17: Varying mixing ratios versus porosities

Figure 3.17 shows the relationship between the mixing ratio variation and porosity of PU foam.

3.3.3.2 Porosities of Varying Pre-Heat Temperature – 50:50 Mixing Ratio

The results observed for the porosity of PU foams produced at various pre-heat temperatures is illustrated in Table 3.5. From the results, it can be observed that the porosity increases from 33.3% at 20°C up to 45.2% at 60°C and decreases up to 37.3% at the earmarked 100°C. Even though this is not directly proportional to the density plot shown in Figure 3.18, there is a trend which confirms that the porosity increases with decreasing density and vice versa in relation to the pre-heat temperature as in Figure 3.16. The increase of porosity from 20°C pre-heat temperature indicates a loss of strength when the temperatures of the PU chemicals were pre-heated before mixing.

Table 3.5: Porosities of varying pre-heat temperature

Pre-Heat Temp (°C)	Porosity (%)				Range	STDEV
	1	2	3	Average (%)		
20	33.4	33.0	33.5	33.3	0.3	0.26
30	38.4	37.2	36.9	37.5	0.8	0.79
40	44.3	43.5	43.6	43.8	0.4	0.44
50	45.0	44.9	44.5	44.8	0.3	0.26
60	45.4	45.1	45.1	45.2	0.1	0.17
70	42.9	41.5	41.3	41.9	0.8	0.87
80	39.0	39.5	38.5	39.0	0.5	0.50
90	37.4	38.3	38.8	38.0	0.7	0.71
100	37.3	37.6	37.0	37.3	0.3	0.30

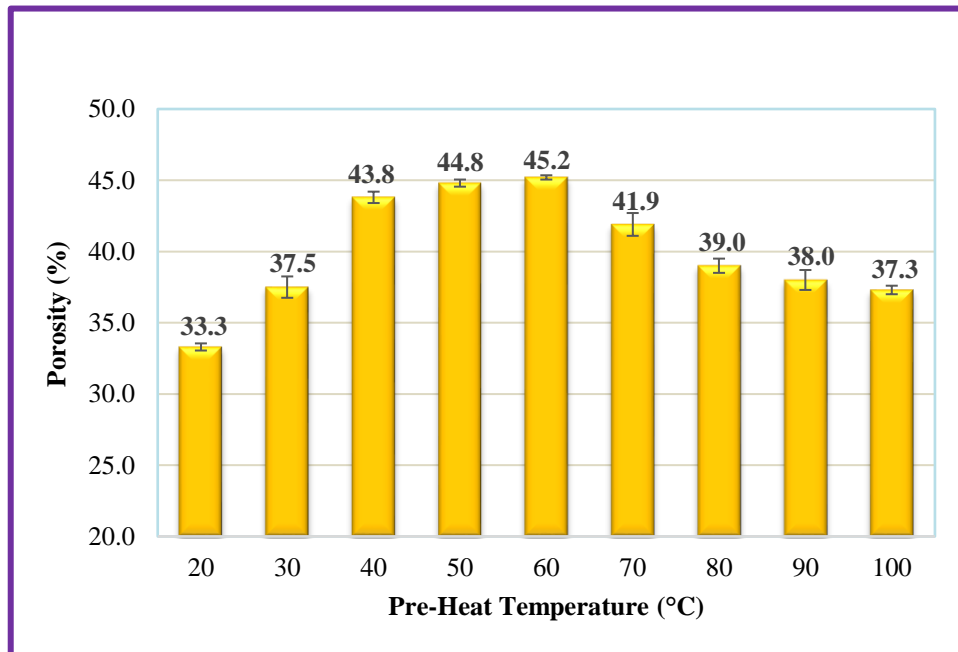


Figure 3.18: Porosities versus varying pre-heat temperature

Figure 3.18 shows the relationship between the pre-heat temperature and porosity of PU foam from 20°C to 100°C.

3.3.4 Comparison of Structures

3.3.4.1 Structures of Different Mixing Ratios and Pre-Heat Temperature

The images obtained from the SEM (Figure 3.19) for the 4 mixing ratios considered were captured at the same scale for fair and accurate comparisons. It could be observed that there is a clear distinction between the structures in the restricted (foaming against the mould walls) foaming direction and that in the free foaming directions. The microstructures of the foams in the free foaming direction are more compact and well arranged than those in the restricted foaming direction. For example the microstructures of the 40:60 and 45:55 foams looks more compact and uniformly interlinked in the free foaming direction than in the restricted foaming direction. The 50:50 and the 55:45 mixings ratios exhibited almost the same characteristics.

The SEM images shown in Figure 3.20 show that the scaffold structure of the 50:50 PU foam varies considerably with increasing pre-heat temperature. The results also show that from 20°C to 40°C, the size of the pores of the foam increases which most likely corresponds to the increase of porosity and decrease of density. The pores of the 50°C specimen were marginally greater in size than the specimen pre-heated to 40°C but also slightly smaller in size than the 60°C specimen, again, indicating an increase in porosity and a corresponding decrease in density. The pore size reduction continues until 100°C which indicates a decreasing trend of porosity and an increasing trend of density of the PU foam from 60°C pre-heat temperature to 100°C. With reference to section 2.12.1, all the foams produced could be suggested to be open cell foams.

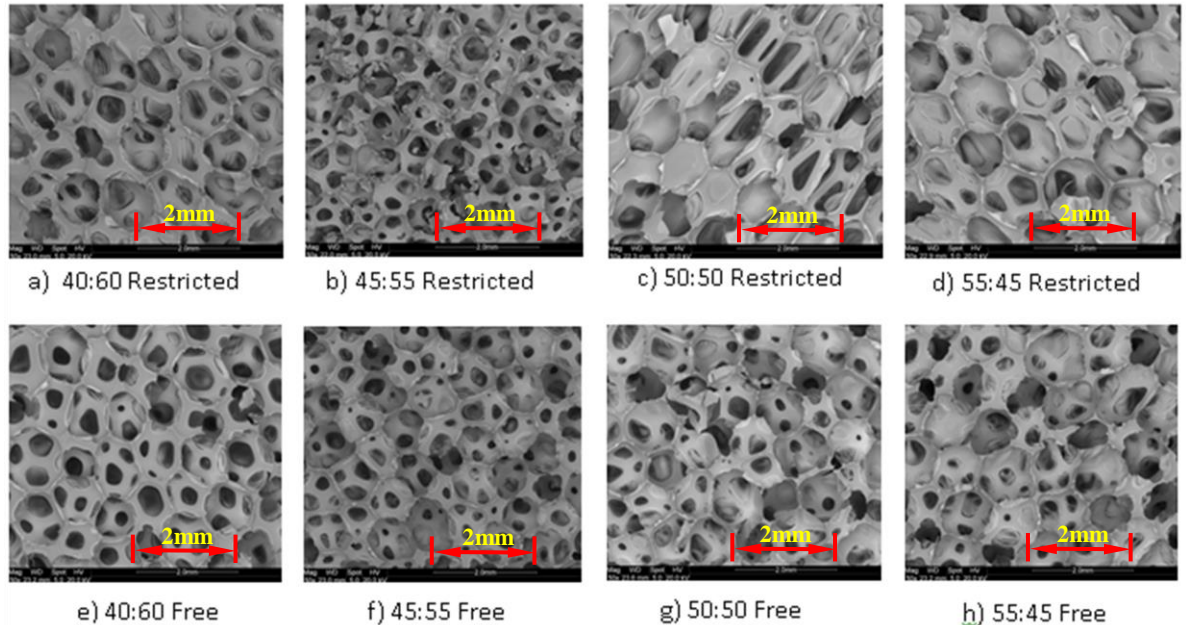


Figure 3.19: Structures of foam with varying mixing ratios in different mixing directions

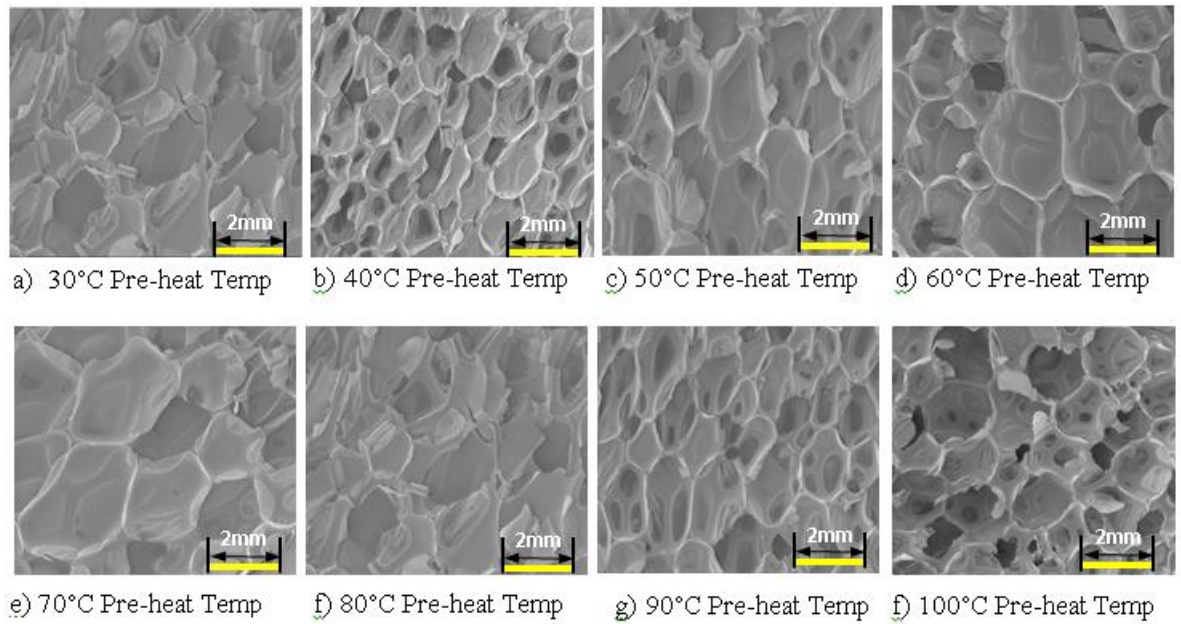


Figure 3.20: Structures of PU foam for 50:50 mixing ratio at varying pre-heat temperatures

3.3.5 Tensile Test Results

3.3.5.1 Tensile Stress for Varying Mixing Ratio

From the results obtained from the tensile testing (Figure 3.21), the average tensile strength obtained for 40:60 mixing ratio in the restricted foaming direction was 590 kPa whilst that obtained in the free foaming direction was 834 kPa. The free foaming direction therefore indicates a 41% increase in strength when compared to the restricted foaming direction (Table 3.6). The average tensile strength for the 45:55 mixing ratio in the restricted foaming direction was 496 kPa whilst that in the free foaming direction was 912 kPa (Figure 3.22), indicating a 45.6% increase in tensile strength (Table 3.6). The average tensile strength for the 50:50 mixing ratio in the restricted foaming direction was 353 kPa whilst that obtained in the free foaming direction was 626 kPa (Figure 3.23), giving an average increase in tensile strength of 77% (Table 3.6). The average tensile strength for the 55:45 mixing ratio in the restricted foaming direction was 345 kPa whilst that in the free foaming direction was 578 kPa (Figure 3.24), indicating an average increase in tensile strength of 67.5% (Table 3.6). Therefore, using the 50:50 (50% polyol and 50% diisocyanate respectively) mixing ratio as the reference, it could be established that the tensile strength increased when the percentage of diisocyanate was increased to 55% with the polyol decreased to 45% (45:55 mixing ratio). However, as the diisocyanate was increased to 60% and the polyol was decreased to 40%, even though the tensile strength was more than that of the 50:50 mixing ratio, it was less than that of the 45:55 mixing ratio.

The superimpositions of the plots of tensile strength of all the four mixing ratios in free and restricted foaming directions are illustrated in Figure 3.25 and Figure 3.26 respectively. The graphs clearly show that the gradient increases with increasing diisocyanate component of the mixing ratio. The graphs of Figure 3.21 – Figure 3.24 indicate that all the curves for the free foaming directions have higher gradients than the restricted foaming directions. The plot of tensile strengths against various mixing ratios is also plotted in Figure 3.27.

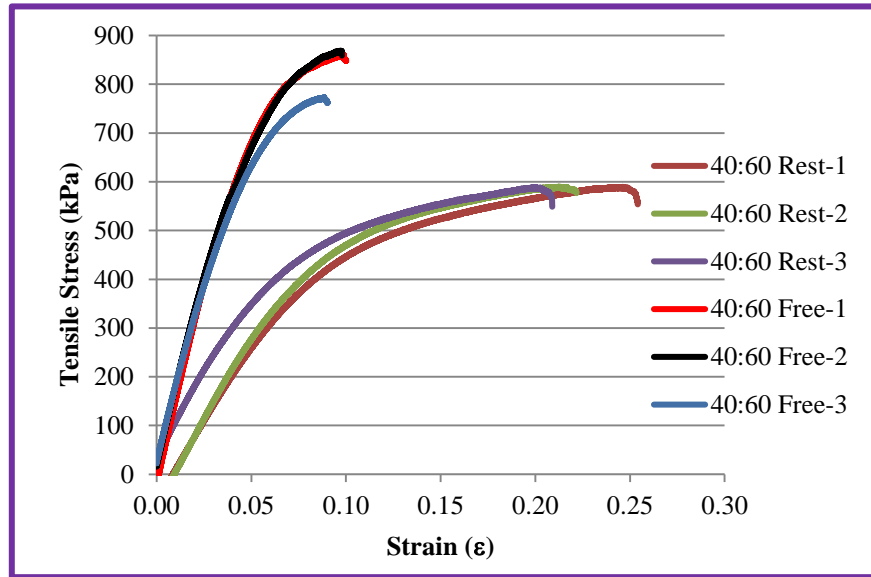


Figure 3.21: Tensile Tests for 40:60 Mixing Ratio

Figure 3.21 shows the tensile stress/strain graph for 40:60 mixing ratio for both free and restricted foaming directions. Three plots each of the two directions were plotted on the same graph to compare the difference.

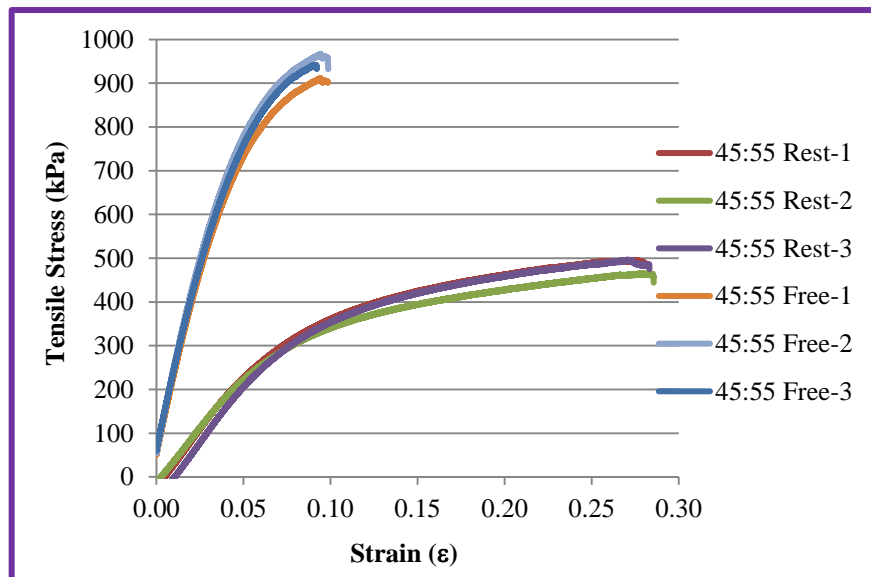


Figure 3.22: Tensile Tests for 45:55 Mixing Ratio

Figure 3.22 shows the tensile stress/strain graph for 45:55 mixing ratio with three curves each for both free and restricted foaming directions.

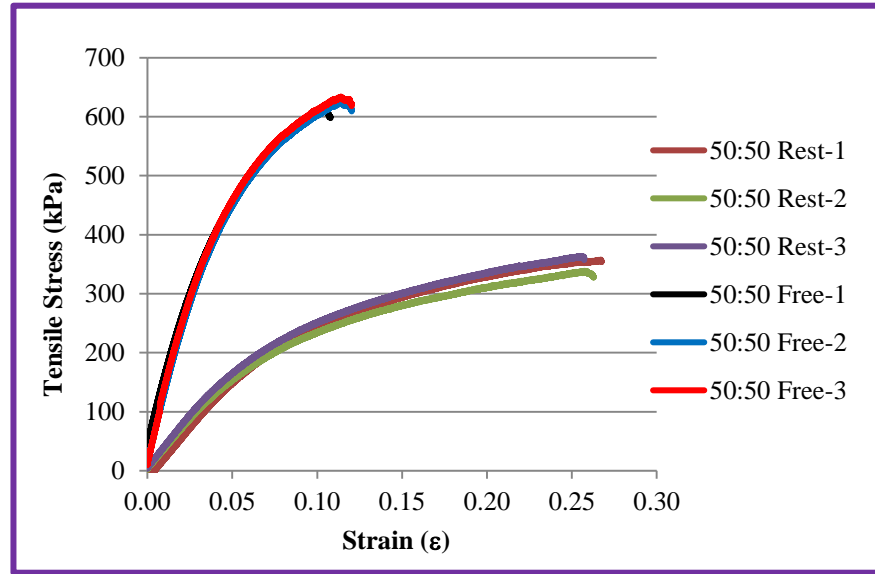


Figure 3.23: Tensile stress for 50:50 mixing ratio

Figure 3.23 shows the tensile stress/strain graph for 50:50 mixing ratio with three curves each for both free and restricted foaming directions.

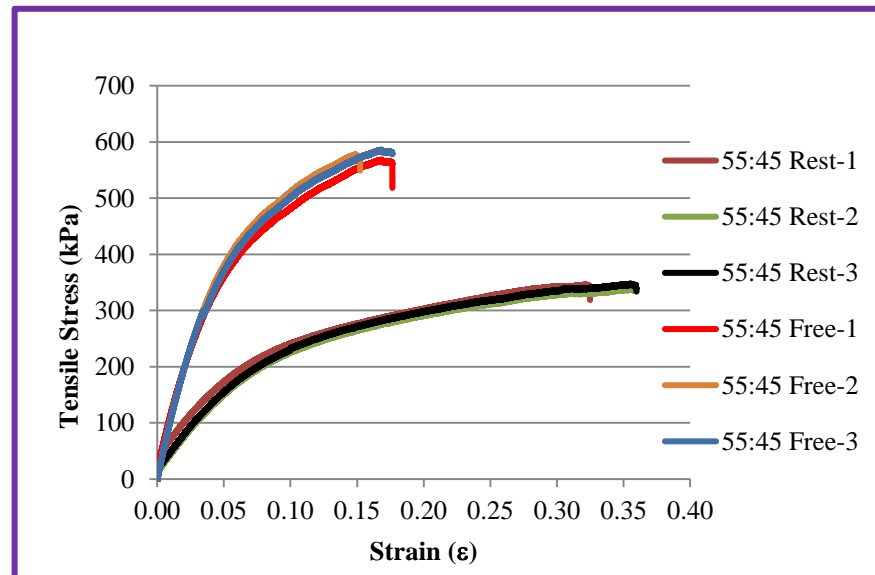


Figure 3.24: Tensile tests for 55:45 mixing ratio

Figure 3.24 shows the tensile stress/strain graph for 55:45 mixing ratio with three curves each for both free and restricted foaming directions.

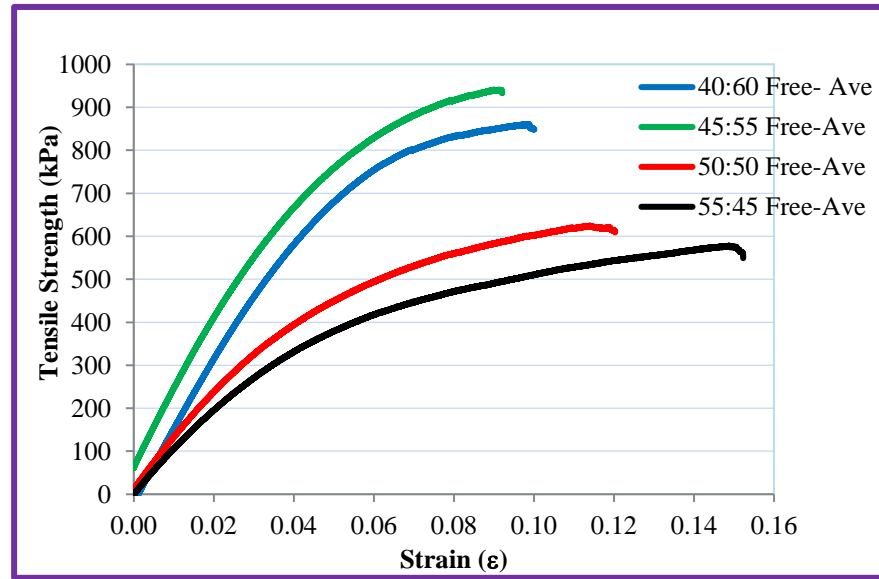


Figure 3.25: Tensile strength of varying mixing ratio in free foaming direction

Figure 3.25 shows the average tensile stress/strain curves of all the four mixing ratios. These were plotted on the same graph to compare their behaviours.

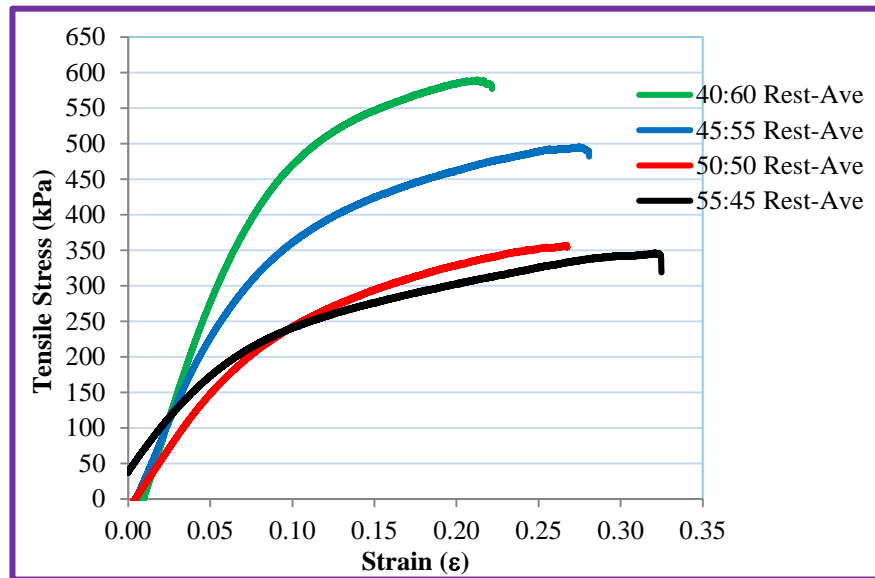


Figure 3.26: Tensile strength of varying mixing ratio in free foaming direction

Figure 3.26 shows the average tensile stress/strain curves of all the four mixing ratios in the restricted foaming direction. These were plotted on the same graph to compare their behaviours.

Table 3.6: Table of tensile strength for PU in both free and restricted foaming directions

Mixing Ratio	Tensile Strength (kN/m ²)	Tensile Strain (ε)	Tensile Strength (kN/m ²)	Tensile Strain (ε)	Tensile Strength (kN/m ²)	Tensile Strain (ε)	Ave Tensile Strength (kN/m ²)	Range	STDEV	Ave Tensile Strain (ε)
	1		2		3					
40:60 Free	860.4	0.099	869.0	0.097	773.2	0.089	834	47.9	53.0	0.095
40:60 Res	589.7	0.246	590.0	0.213	589.1	0.200	590	0.4	0.5	0.220
45:55 Free	912.0	0.094	967.0	0.094	941.0	0.091	940	27.5	27.5	0.093
45:55 Res	496.0	0.275	464.8	0.278	497.0	0.271	486	16.1	18.3	0.275
50:50 Free	617.9	0.106	625.0	0.114	634.0	0.114	626	8.1	8.1	0.111
50:50 Res	358.0	0.267	339.0	0.258	363.0	0.225	353	12.0	12.7	0.250
55:45 Free	569.0	0.168	578.0	0.149	586.5	0.168	578	8.8	8.8	0.162
55:45 Res	346.6	0.321	340.0	0.355	348.0	0.355	345	4.0	4.3	0.344

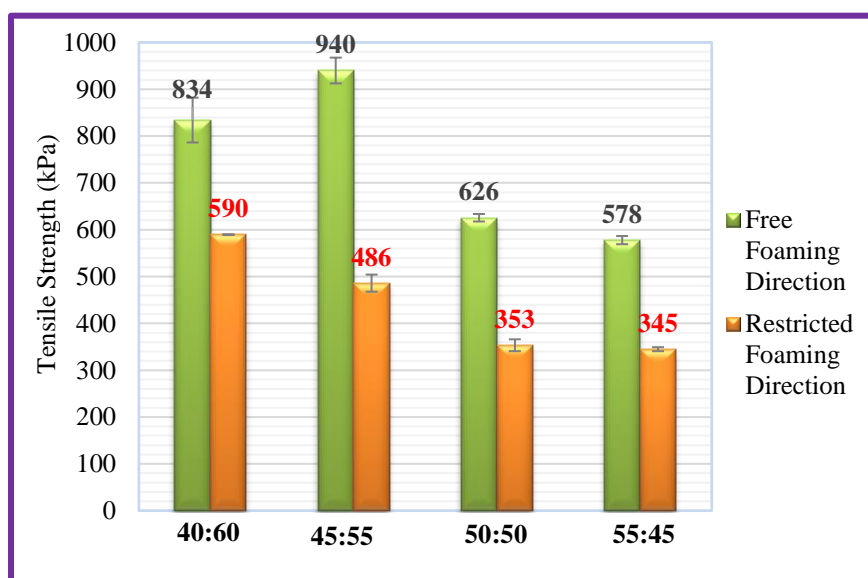


Figure 3.27: Comparison of tensile strengths in different foaming directions for different mixing ratios

Figure 3.27 shows the strength comparison of free foaming and restricted foaming directions of g mixing ratios of PU foam

3.3.5.2 Tensile Strength for Varying Pre-Heat Temperature

The tensile strength obtained when the mixing ratio was maintained at 50:50 and pre-heated from 20°C to 100°C is illustrated in Table 3.7

Table 3.7: Tensile strengths and strains of varying mixing ratio and different foaming directions

Pre-heat Temp (°C)	Free Foaming Direction (y)				Restricted Foaming Direction (x)			
	Average Tensile Strength (kPa)	Strain (ϵ)	Range	STDEV	Average Tensile Strength (kPa)	Strain (ϵ)	Range	STDEV
20	625.6	0.113	8.1	8.07	430	0.243	12.0	13.08
30	582.0	0.106	7.5	7.94	356	0.160	13.0	13.10
40	465.0	0.090	4.5	4.58	322	0.191	7.5	7.55
50	468.3	0.078	8.7	9.64	291	0.222	14.0	14.93
60	508.5	0.066	5.5	5.94	321	0.224	6.5	7.00
70	501.0	0.047	7.7	8.17	246	0.125	24.5	26.29
80	491.3	0.061	19.3	20.01	287	0.172	14.5	15.72
90	523.4	0.053	10.3	10.51	292	0.171	14.5	15.72
100	547.5	0.068	18.3	19.00	342	0.201	18.0	19.97

Figure 3.28 shows five random selected stress/strain curves of the 50:50 mixing ratio of PU foam from 20°C to 100°C in the free foaming direction. The detailed tensile strengths are illustrated in Table 3.7. and plotted in Figure 3.30. From the Table and the graph, when the pre-heat temperature was increased from room temperature (approximately 20°C) to 30°C, the tensile strength reduced from 625.6 kPa with a corresponding strain of 0.113 to 582 kPa with a corresponding strain of 0.106 indicating a decreased in strength of 6.6%. A further increase of pre-heat temperature to 40°C realised a sharp drop of tensile strength to 465.5 kPa indicating 25.3% reduction in strength compared to the strength at 20°C. The tensile strength at 40°C increased gradually to 468 kPa at 50°C and a strain of 0.078 and to 509 kPa with a corresponding strain of 0.066 at 60°C. It decreased again gradually to 491.3 kPa at 80°C and a strain of 0.061. This increased slowly to 548 kPa and corresponding strain of 0.068 at 100°C.

Even though the stress and strain behaviour changed as the pre-heat temperature was altered, the trend was not the same as the ones in free foaming direction.

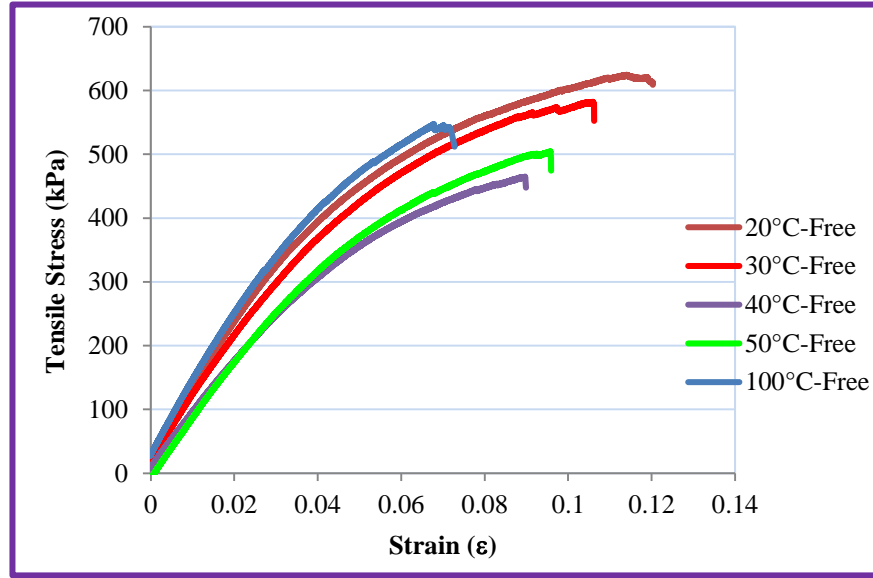


Figure 3.28: Tensile stress for varying pre-heat temperature for free foaming direction

Figure 3.29 shows five random selected stress/strain curves of the 50:50 mixing ratio of PU foam from 20°C to 100°C in the restricted foaming direction. The detailed tensile strengths are illustrated in Table 3.7. and Figure 3.30. According to the graph, the sample with the highest tensile strength was the 20°C pre-heat with a tensile strength of 430 kPa and a strain of 0.243. This was followed by a sharp drop to 356 kPa with a corresponding strain of 0.160, indicating a 17.2% reduction of strength at 30°C. The strength was decreased to 322 kPa and a strain of 0.191 at 40°C and a further decreased to 291 kPa and a strain of 0.222 kPa at 50°C. The tensile strength increased to 321 kPa with a 0.224 strain at 60°C. The fluctuation of tensile strength continued until at a strength of 342 kPa with a corresponding strain of 0.201 at 100°C.

Even though the stress and strain behaviour changed as the pre-heat temperature was varied, the trend was not the same as the free foaming direction one.

In all cases, comparing the results obtained for the free foaming and the restricted foaming directions, it could be realised that all the tensile strengths in the free-foaming directions are higher than their corresponding ones obtained from restricted foaming. These confirm the results obtained from the varying mixing ratios. The strain as plotted on both graphs (Figure 3.28 and Figure 3.29) show that once the resins are pre-heated the

strain reduced, except the 30°C which had strain more than the 20°C for the restricted foaming direction. All the strains recorded are less for the free foaming direction than the restricted foaming direction. The comparison of tensile strengths for restricted and free foaming directions at varying pre-heat temperature is illustrated in Figure 3.30.

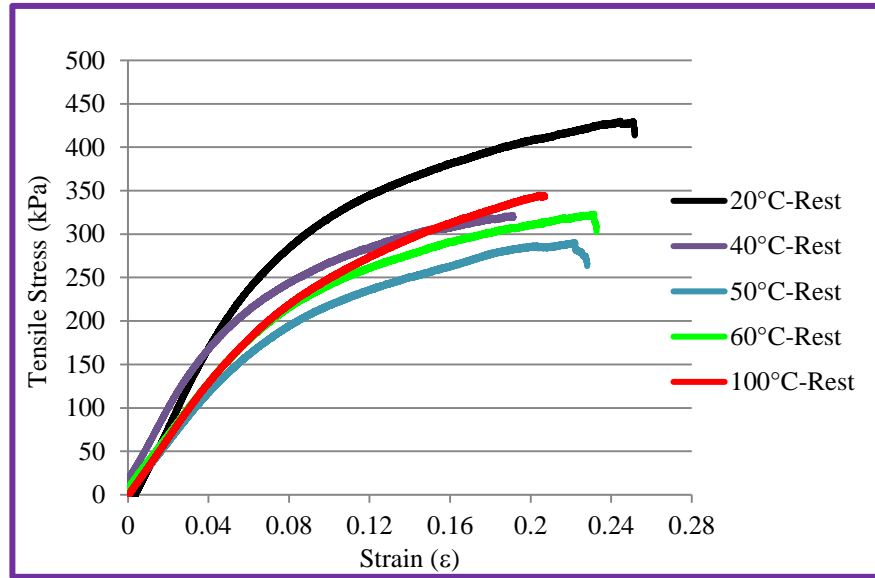


Figure 3.29: Tensile stresses for varying pre-heat temperatures in restricted foaming direction

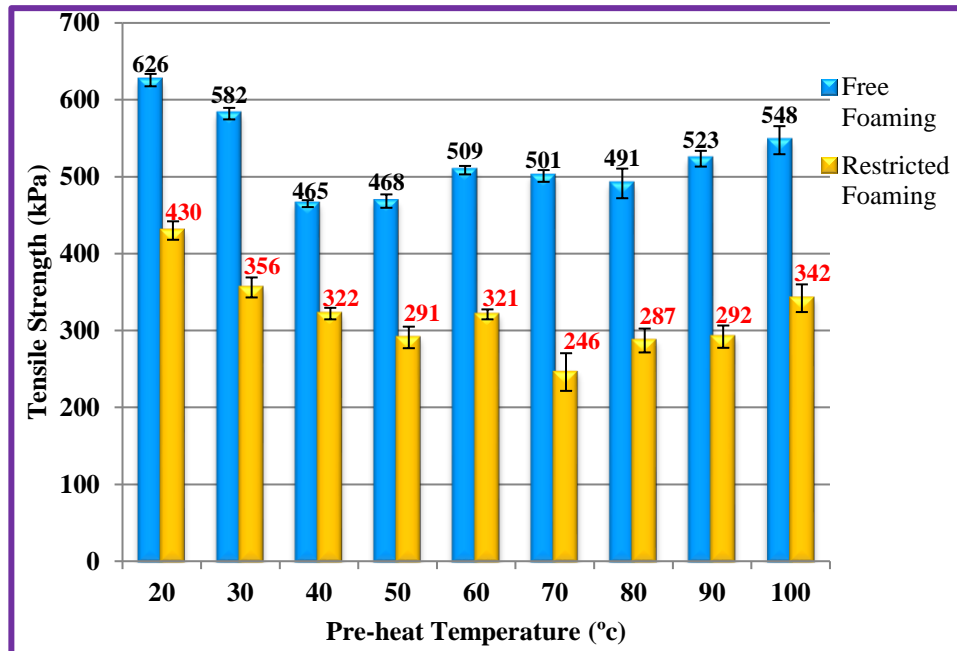


Figure 3.30: Tensile strength of varying pre-heat temperature for restricted and free foaming directions

3.3.5.3 Recommendation

From the results observed, it could be recommended that, where the applications do not require much tensile strength and fall within the stated range of strengths, pre-heating the PU resins before mixing would be of great advantage to save a lot of foaming/curing time which would make the material suitable for high speed process applications. The tensile strength can further be improved with the addition of other ingredients depending on the intended application.

3.3.6 Compressive Test Results

3.3.6.1 Varying Mixing Ratio

The strength of the foams in compression was measured up to the yield point. The results obtained for the compressive stresses in the restricted and free foaming directions for all the mixing ratios considered are outlined in Figure 3.31–Figure 3.34. Figure 3.35 shows the average compressive stress superimposition of all the free foaming directions and Figure 3.36 shows the average compressive stress superimposition of all the restricted foaming directions.

The compressive strengths for the free foaming and restricted foaming are illustrated in Figure 3.37 and Table 3.8. From the results, the average compressive strength for the 40:60 mixing ratio in the restricted foaming direction was 360 kPa, whilst that for the free foaming direction was 470 kPa, representing a 30.6% increase in compressive strength. The average compressive strength for the 45:55 mixing ratio in the restricted foaming direction was 262 kPa whilst that obtained for the free foaming direction was 388 kPa, indicating 48% increase in strength. The compressive yield strength for 50:50 mixing ratio was 176 kPa in the the restricted foaming direction and that in the free foaming direction was 315 kPa, amounting to 80% increase in compressive strength. The average compressive strength for the 55:45 mixing ratio in the the restricted foaming direction was 144 kPa whilst that in the free foaming direction was 205 kPa, which is 42.4% increase in compressive strength. The results obtained for the compressive stresses indicated that the strength of the 45:55 mixing ratio was more than that of the 50:50 mixing ratio and that of the 55:45 mixing ratio was less than that of the

50:50 mixing ratio. Unlike the tensile strengths, the average compressive strength of the 40:60 mixing ratio was more than that of the 45:55 mixing ratio.

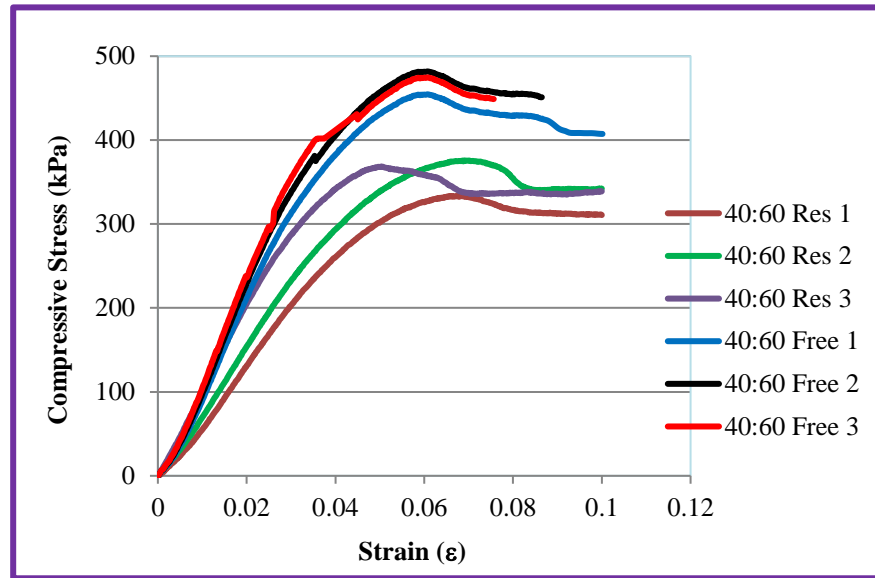


Figure 3.31: Compressive stress for 40:60 mixing ratio

Figure 3.31 show the compressive stress/strain graph for 40:60 mixing ratio for both free-foaming and the restricted foaming directions. Three plots each of the two directions were plotted on the same graph to compare the difference.

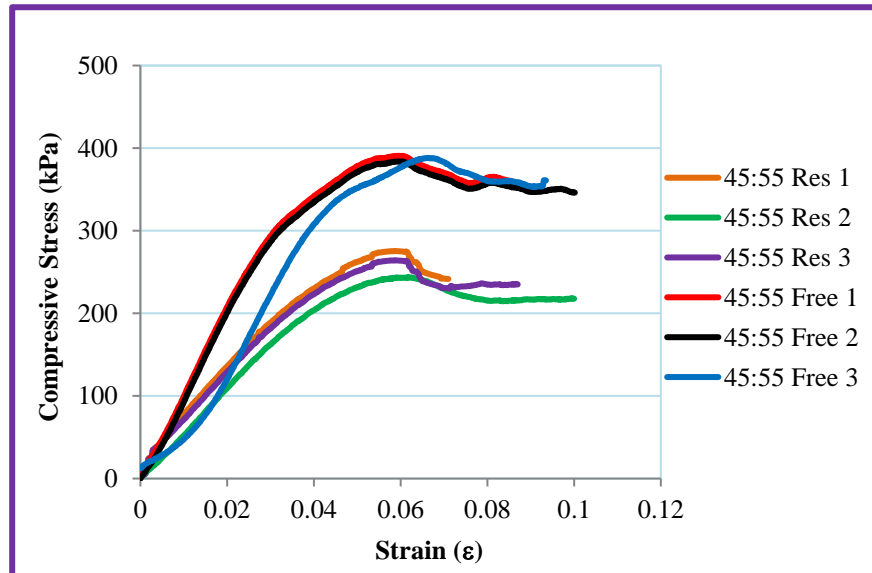


Figure 3.32: Compressive stress for 45:55 mixing ratio

Figure 3.32 show the compressive stress/strain graph for 45:55 mixing ratio for both free-foaming and the restricted foaming directions. Three plots each of the two directions were plotted on the same graph to compare the difference.

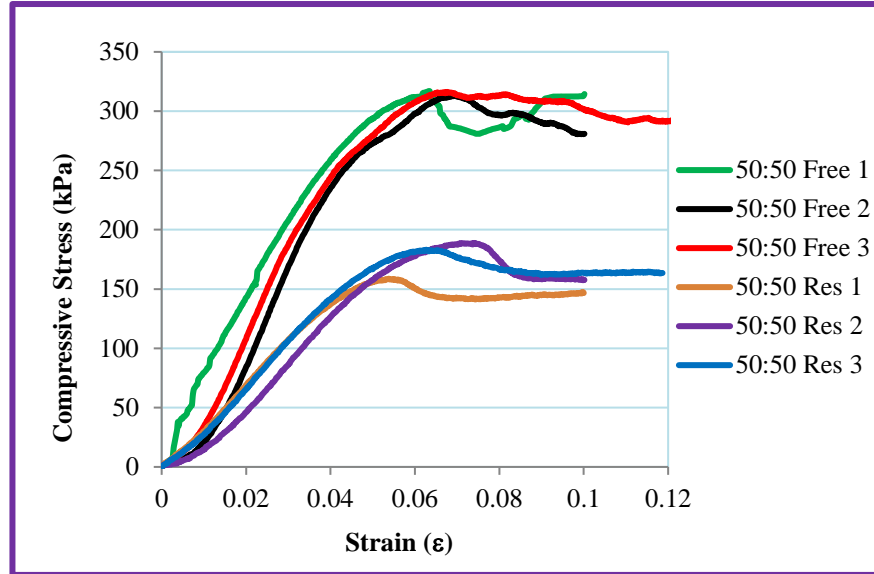


Figure 3.33: Compressive stress for 50:50 mixing ratio

Figure 3.33 show the compressive stress/strain graph for 55:45 mixing ratio for both free-foaming and the restricted foaming directions. Three plots each of the two directions were plotted on the same graph to compare the difference.

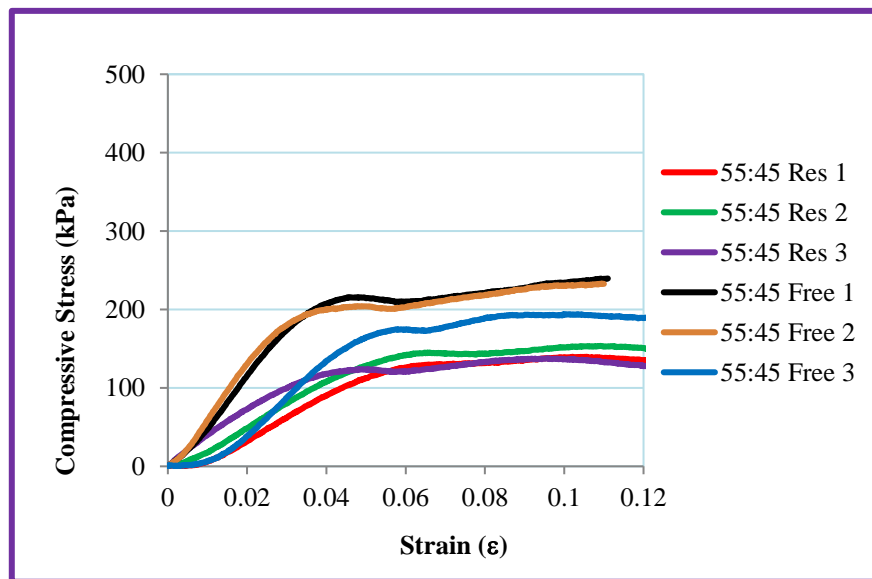


Figure 3.34: Compressive stress for 55:45 mixing ratio

Figure 3.34 show the compressive stress/strain graph for 50:50 mixing ratio for both free-foaming and the restricted foaming directions. Three plots each of the two directions were plotted together to compare the difference.

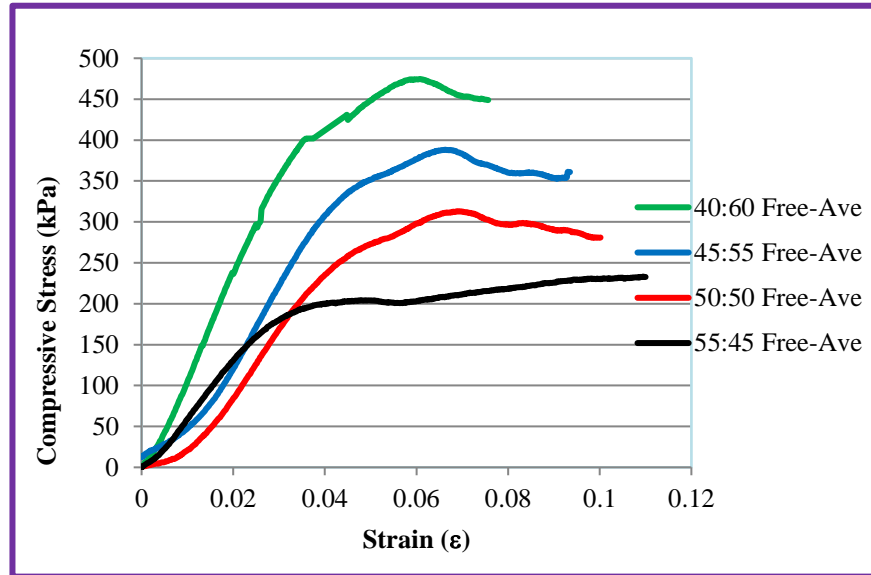


Figure 3.35: Compressive stresses at varying mixing ratio for free foaming direction

Figure 3.35 shows compressive stresses of three sample each of the four mixing ratios considered in the longitudinal or foaming in the direction of open end of the mould.

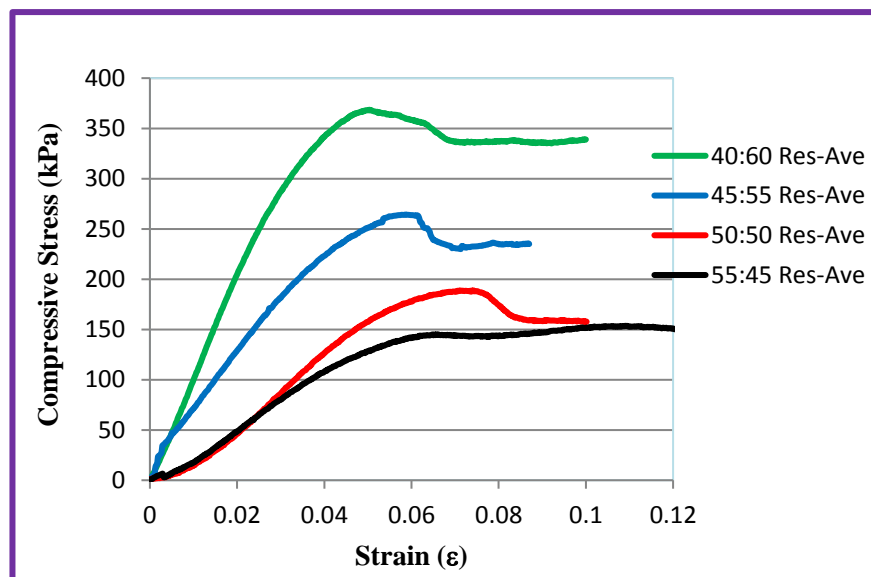


Figure 3.36: Compressive stresses at varying mixing ratio for restricted foaming direction

Figure 3.36 shows compressive stresses of three sample each of the four mixing ratios considered in the transverse or foaming against the walls of the mould.

Table 3.8: Summary of compressive strengths for varying mixing ratio in x and y directions

Mixing ratio	Compressive Strength (kPa)	Compressive Strain (ϵ)	Compressive Strength (kPa)	Compressive Strain (ϵ)	Compressive Strength (kPa)	Compressive Strain (ϵ)	Average Comp Strength	Range	STDEV	Average Compressive Strain (ϵ)
	1		2		3					
40:60 Free	474.6	0.061	481.8	0.061	454.5	0.061	470.3	13.6	14.1	0.061
40:60 Res	333.9	0.068	376.0	0.070	368.6	0.050	359.5	21.1	22.5	0.063
45:55 Free	391.0	0.060	384.0	0.060	388.0	0.066	387.7	3.5	3.5	0.062
45:55 Res	276.0	0.059	244.0	0.062	264.4	0.059	261.4	16.0	16.2	0.060
50:50 Free	316.9	0.064	313.0	0.069	316.3	0.068	315.4	2.0	2.1	0.067
50:50 Res	158.5	0.054	188.9	0.074	183.2	0.063	176.9	15.2	16.1	0.064
55:45 Free	215.8	0.048	204.3	0.048	193.9	0.100	204.7	10.9	10.9	0.065
55:45 Res	139.7	0.102	153.7	0.109	137.9	0.096	143.8	7.9	8.6	0.102

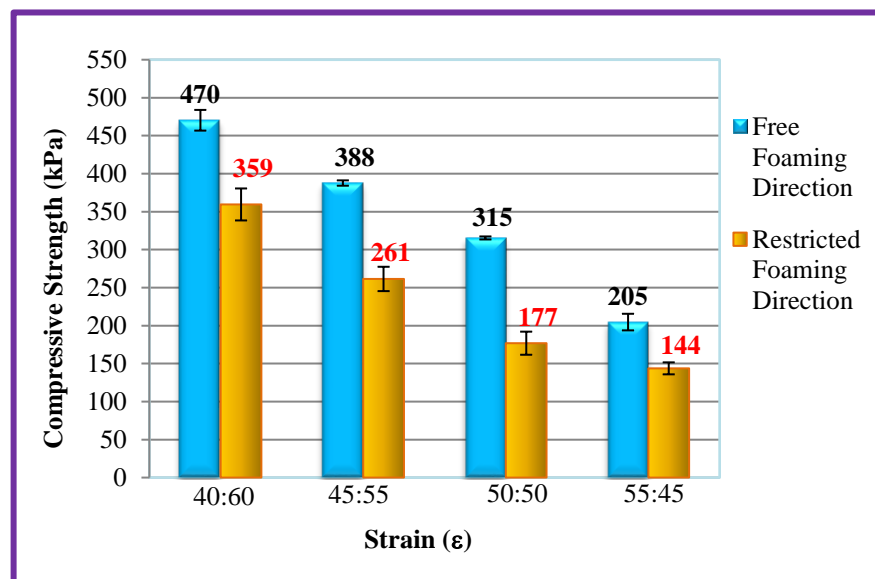


Figure 3.37: Comparison of tensile strength in different foaming directions for different mixing ratios

Figure 3.37 shows the comparison of compressive strengths in free and restricted foam-ing directions for varying mixing ratios.

3.3.6.2 Compressive Stress for Varying Pre-Heat Temperature at 50:50 Mixing Ratio

Table 3.9 illustrates the compressive strength for foams produced at different pre-heat temperature from 20°C to 100°C for free foaming direction and five random selected stress/strain graph is plotted in Figure 3.38. The foam produced at 20°C pre-heat temperature with 315 kPa tensile strength and strain of 0.065 was used as reference. As stated in the previous section, the compressive strengths quoted for the compression analysis were the yield strengths. At 30°C the compressive strength was 330 kPa which was 15 kPa or 4.8% increase in strength compared to the strength at 20°C with a strain of 0.084. The compressive strength at 40°C was 368 kPa indicating an increase of 53 kPa or 16.8% compared to the 20°C compressive strength with corresponding strain of 0.055. At 50°C the compressive strength was 388 kPa and this indicated an increase in strength of 73 kPa or 16.8% compared to the compressive strength at 20°C and a strain of 0.087. The compressive strength at 60°C was 319 kPa which was an increase in strength of 4 kPa or 1.3% compared to the compressive strength at 20°C pre-heat temperature. Even though it was less than the compressive strength at 50°C, it was still more than the compressive strength at 20°C. The compressive strength further increased to 357 kPa at 70°C pre-heat temperature which indicated an increase in compressive strength of 42 kPa or 13.3% compared to the strength at 20°C pre-heat temperature and strain of 0.094. The compressive strength at 80°C was 59 kPa or 18.7% less compared to the compressive strength at 20°C and a strain of 0.094. The compressive strength for the 90°C pre-heat temperature was 283 kPa indicating a reduction of 32 kPa or 10.2% and a corresponding strain of 0.082. At 100°C, the compressive strength was 286 kPa which is 29 kPa or 9.2% decrease in strength when compared to the strength at 20°C pre-heat temperature with a strain of 0.065. This was an increase of 3 kPa when compared to the strength at 90°C. From the analysis, it could be realised that when the pre-heat temperature was altered from 20°C, the compressive strengths did not have a consistent trend of variation with the pre-heat temperature. The least compressive strength recorded was 256 kPa at 80°C pre-heat temperature foam.

Table 3.9: Compressive strengths and strain for pre-heat temperature in free-foaming direction

Pre-heat Temp (°C)	Strength (kPa)	Strain	STDEV	Range
20	315	0.065	11.8	11.5
30	330	0.084	11.1	11.0
40	368	0.055	12.2	11.0
50	388	0.087	7.5	7.5
60	319	0.064	19.3	18.0
70	302	0.078	7.9	7.5
80	256	0.094	10.6	10.0
90	283	0.082	7.0	6.5
100	286	0.068	7.0	6.5

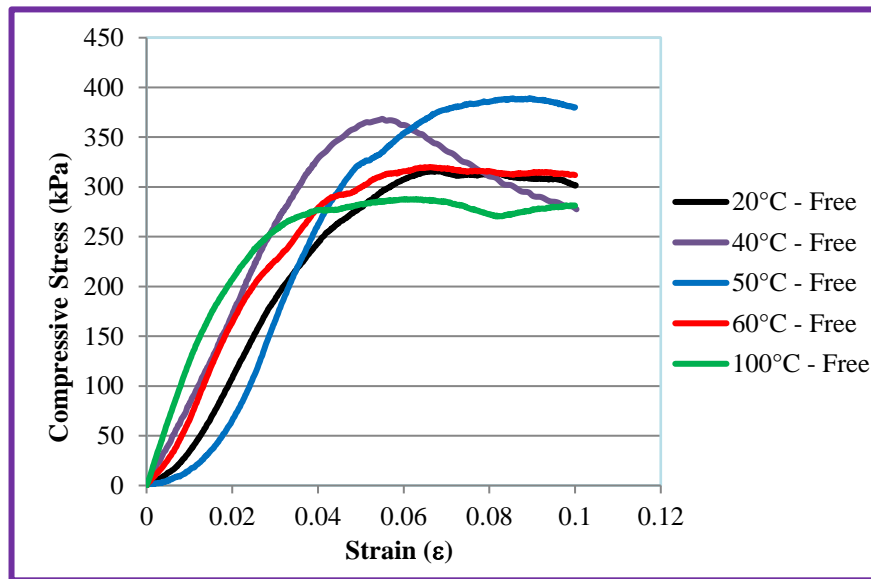


Figure 3.38: Compressive stress against strain for varying pre-heat temperature in restricted foaming direction

The results for compressive stress and strain for restricted foaming direction for pre-heated from 20–100°C is illustrated in Figure 3.40. Unlike the free foaming direction, the compressive strength decreased with initial increased in pre-heat temperature up to 211 kPa and a strain of 0.064 at 40°C. This was increased gradually to 232 kPa with a corresponding strain of 0.063 at a pre-heat temperature of 60°C. It then decreased again to 241 kPa with a strain of 0.064 at 80°C and increased gradually to 271 kPa and a

strain of 0.066 at 100°C. The detailed compressive strengths and strain at yield is illustrated in the Table 3.10.

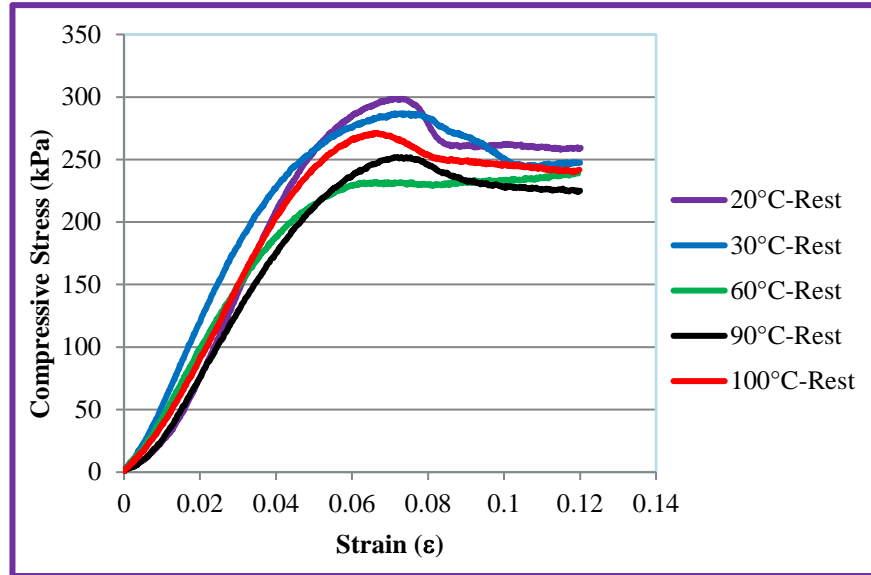


Figure 3.39: Compressive stress against strain for varying pre-heat temperature in restricted foaming direction

Table 3.10: Compressive Strengths and strain for pre-heat temperature in restricted foaming direction

Pre-heat Temp (°C)	Strength (kPa)	Strain	STDEV	Range
20	298	0.071	6.2	6.0
30	287	0.074	12.2	11.0
40	211	0.064	15.6	14.0
50	230	0.066	12.3	11.5
60	232	0.063	8.7	8.0
70	227	0.098	9.5	8.5
80	241	0.064	12.2	11.0
90	251	0.073	7.9	7.5
100	271	0.066	14.8	13.5

Comparing the results obtained for the free-foaming direction to the restricted foaming direction, it could be realised that even though at all pre-heat temperatures the compressive strengths in the restricted foaming directions were less than those in the free foam-

ing directions (Figure 3.40) as was the case of previous analysis, initial increase in pre-heat temperature increased the compressive strengths for the free-foaming direction, whilst in the case of the restricted foaming direction the initial increase in pre-heat temperature resulted in decreased in compressive strengths. In the case of the restricted foaming directions all the values obtained from 30°C to 100°C were substantially far away from the compressive strengths obtained for the 20°C.

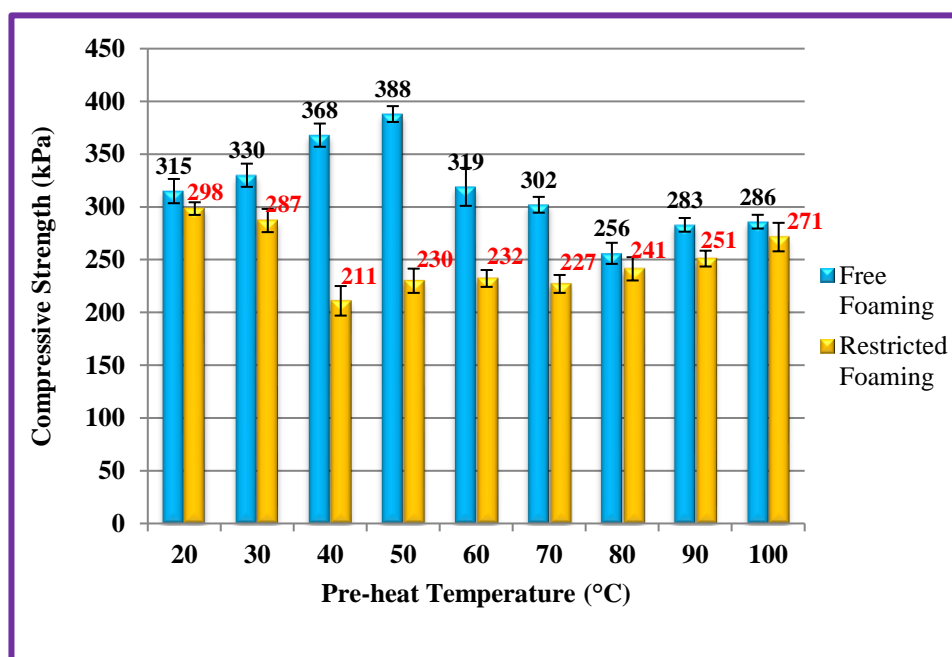


Figure 3.40: Compressive strengths for varying pre-heated temperature for both free and restricted foaming directions.

3.3.6.3 Effect of Pre-Heat Temperature on Foaming Time

Results of foaming time versus pre-heat temperature are shown in Figure 3.41. The results indicate that the foaming time at the standard temperature of 20°C was 452 seconds. This was reduced by increasing the pre-heat temperature down to 54 seconds at 100°C pre-heat temperature, indicating 88% reduction in foaming/curing time. From the graph, there is a trend that the foaming time reduces as the pre-heat temperature increases (Table 3.11), but the decrease in foaming time above 80°C pre-heat temperature is relatively insignificant.

Table 3.11: Foaming Time for varying pre-heat temperature

Pre-Heat Temp (°C)	Foaming time (secs)				Range	STDEV
	1	2	3	Average		
100	52	52	58	54	3.0	3.5
90	57	54	60	57	3.0	3.0
80	64	66	68	66	2.0	2.0
70	98	97	93	96	2.5	2.6
60	130	132	128	130	2.0	2.0
50	145	147	152	148	3.5	3.6
40	181	184	190	185	4.5	4.6
30	221	222	229	224	4.0	4.4
20	457	451	448	452	4.5	4.6

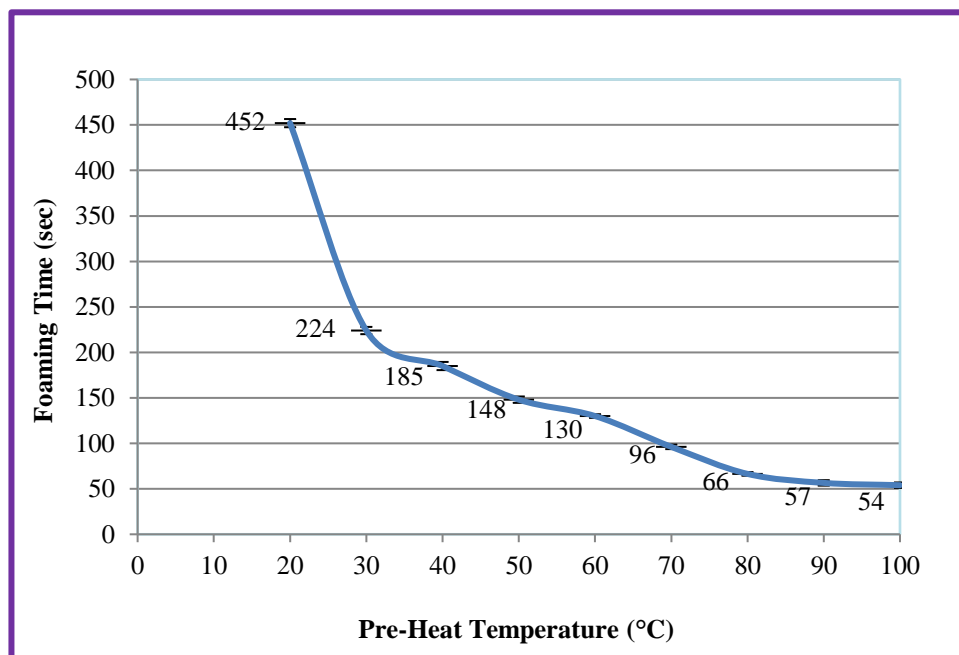


Figure 3.41: Pre-heat temperature against foaming time

3.3.7 Viscosities of PU Foam Resins at Varying Temperature

The viscosities of the PU resins A and B at varying temperatures are illustrated in Table 3.11 and Table 3.12 for three tests conducted.

Table 3.12: Table viscosity of polyol at different temperatures

POLYOL					
Temperature (°C)	Viscosity (cP)				Range
	1	2	3	Average	
20	712	711	707	710	2.5
30	265	266	264	265	1.0
40	219	220	224	221	2.5
50	207	208	212	209	2.5
60	196	194	198	196	2.0
70	187	183	188	186	2.5
80	179	184	177	180	3.5
90	×	×	×	×	×
100	×	×	×	×	×

Table 3.13: Table of viscosities of diisocyanate at different temperatures

DIISOCYANATE					
Temperature (°C)	Viscosity (cP)				Range
	1	2	3	Average	
20	528	530	547	535	9.5
30	237	239	229	235	5.0
40	191	200	185	192	7.5
50	186	191	181	186	5.0
60	179	181	180	180	1.0
70	177	179	178	178	1.0
80	169	170	174	171	2.5
90	×	×	×	×	×
100	×	×	×	×	×

From the graph of temperature against viscosity (Figure 3.42), it could be realised that at 20°C (assumed room temperature) when the polyol has not been heated at all, the viscosity measured was 710 cP. At heated temperature of 30°C, the average viscosity was 235 cP indicating a drop in viscosity of 445 cP or 62.7% compared to the viscosity at 20°C. The average viscosity measured at 40°C was 221 cP indicating 68.9% decrease compared to the viscosity at 20°C. At 50°C, the viscosity drop was not too different from that measured at 40°C as it recorded 70.6% decreased compared to that at 20°C. The viscosities at 60°C, 70°C, and 80°C were 180 cP, 178 cP, and 171 cP respectively.

Even though the viscosity of the diisocyanate measured at 20°C (535 cP) was far less than that of the polyol at 20°C, the trend was not different as it dropped suddenly to 235 cP indicating 300 cP or 56.1% decreased compared to its viscosity at 20°C. The viscosity measured at 40°C was 192 cP indicating a difference of 343 cP or 64% reduction. The viscosity at 50°C was 186 cP which was 349 cP or 65.2% decreased compared to that at 20°C. The viscosities at 60°C, 70°C, and 80°C were 180c, 178cP, and 171 cP respectively.

The viscosities of the two resins (polyol and diisocyanate) were superimposed on each other as illustrated in Figure 3.43 for comparison. From the graph, it could be realised that above 30°C, there is no significant decrease in viscosity, thereby, ending the heating at 80°C. From the results observed, it could therefore be suggested that reducing the viscosities of the resins for easy flow, 30°C to 40°C is highly recommended.

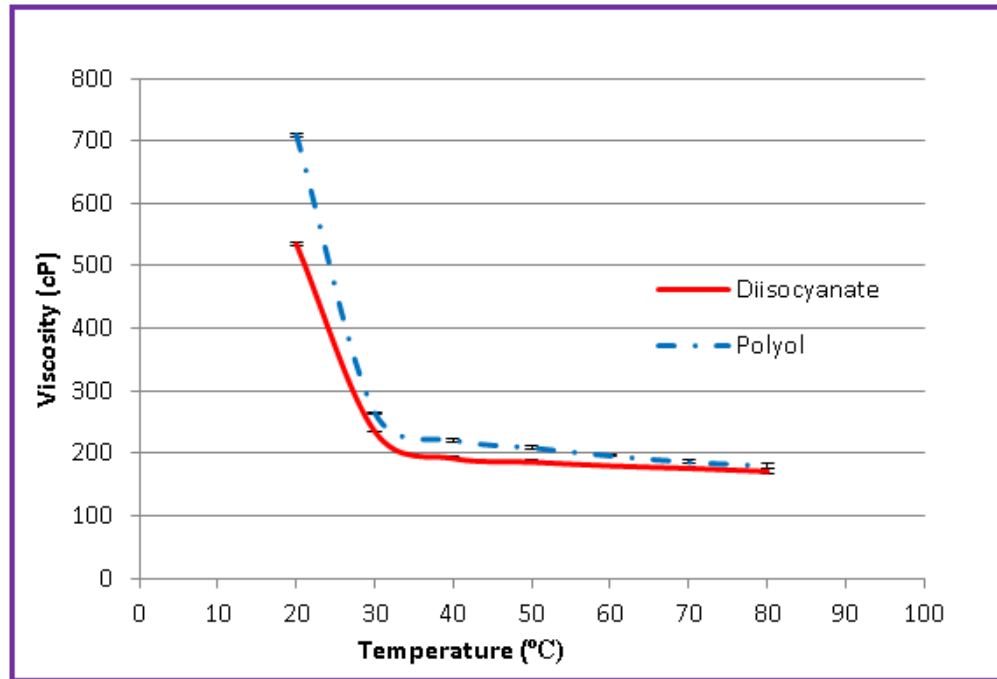


Figure 3.42: Graph of Viscosity against Temperature

It could therefore be said that for both polyol and diisocyanate, the viscosities reduce sharply as the temperature is increased from room temperature to about 50°C and reduce slowly with further increase of temperature. Hence, if a system is to be designed to allow easy flow, between 50°C and 60°C could be used as the basis.

Recommendation

Where compressive yield strength required for a particular application is not high, pre-heat temperature would be of great advantage. This can further be improved with the addition of other ingredients for higher compressive strength applications. This is also indicated on the tensile and compressive stresses graphs that the density of the PU foam upon pre-heating decreases with decreasing strength up to pre-heat temperature of 70°C and improves thereafter up to the earmarked 100°C for this research.

CHAPTER FOUR

MIXING OF POLYURETHANE INSIDE A CHAMBER – DEPOSITION METHOD

4.1 Introduction

This chapter focuses on the modification of X Y Z deposition robot machine (Fisnar F4200N brand) to suit the building of PU foam on the surface of a build platform. The equipment dispenses liquid using compressed air and it is originally designed for medical and laboratory type of environment^[198]. It is used for dosing of points, arcs, and circles, therefore being ideal for sealing, gluing, casting and filling with a resolution of 0.01 mm^[198]. The selection of this equipment was based on pragmatic decision as this was already available and therefore did not need a new arrangement for its acquisition. The suitability of this equipment was based on the information obtained in the experimentation of flow characteristics of individual parts in chapter 3. The X Y Z deposition machine was critically studied and modified to be able to mix PU base resins inside a chamber in the appropriate mixing ratio and dispense it layer by layer to conform to the principle of Additive Manufacturing.

4.2 Methodology

The characteristics of PU foam prepared by hand mixing and cast in moulds were investigated to provide baseline information that could later be compared to PU foam produced by the deposition system designed to be incorporated with the 3D printer for its application. Following the investigation, a similar methodology was used to design the concept of PU foam deposition method which again utilised the research conducted in the literature survey to gather information for the system design.

The deposition system was used to produce samples of foam that were tested using the same procedure applied for the testing of samples obtained by hand mixing and casting

to evaluate the effectiveness of the deposition system by comparing the physical properties of the hand mixed samples to the ones produced by the proposed 3D printed system. Finally, the deposition system was used to fully automate the process of creating tracks using pre-programmed commands issued to a robot that could be examined to determine potential printability of PU foam and the effectiveness of the deposition system.

4.3 Deposition Method for PU Foam Using X Y Z Deposition Robot (Fisnar 4200N brand) - A Proposed System

4.3.1 Requirements of the Proposed System:

- Must allow for the flow and use of liquids
- Must have disposable components wherever there is contact with the combined mixture after curing
- The two individual parts must mix uniformly
- Programmable control
- X, Y, Z axis movements

4.3.2 Printer Selection

The available additive manufacturing technologies were assessed for suitability for this particular application with a printing method being selected to form the basis of the deposition method for PU foam.

An X Y Z liquid dispensing robot which was the available on-site equipment was modified for the dispensing of the PU foam as it stood as the choice to form the basis of the deposition method for the PU foam system. The robot dispenses liquid using compressed air and as stated by the manufacturer, it is originally designed for medical and laboratory type environments^[198], portable (approx. 50 cm in height, width and diameter, 20 kg weight) and enables its use inside a fume cupboard which meant all testing could be carried out safely with no risk of exposure of chemicals to the laboratory occupants. It is used for dosing of points, arcs, and circles, therefore being ideal for seal-

ing, gluing, casting and filling with a resolution of 0.01 mm^[198]. It has a storage capacity for 100 programs, 400,000 points, 4,000 points per program and a working area X/Y/Z of 200 x 200 mm x 50 mm. it dispenses continuous path and point-to point^[198].

4.4 Material Application and Process

Fisnar Deposition Robot uses compressed air to dispense liquids from syringes, which ranges from 0.1 to 7 bar pressure^[199] as required by the application. Liquids can be added to a syringe which is then attached to a pressure source and fixed to the front plate of the robot to dispense the liquid using the robot to control the flow of air into the syringe, thus determining when the liquid is dispensed^[199].



Figure 4.1: Fisnar F4200N X Y Z deposition machine^[196]

4.4.1 Nature of PU Foam Mixture

When PU resins are mixed and allowed to foam, the mixture expands and quickly fills cavities wherever used and any component that the combined mixture passes through are likely to become completely filled with semi liquid PU foam and solidify when it had completely foamed and cured. As a result, the deposition system required disposable parts from the point of mixing onwards through the system.

4.4.2 Uniform Mixing of the Individual Parts

For the deposition system to be re-usable, mixing the two main parts of the PU foam together needed to occur in a disposable part of the system that could be removed and replaced without requiring any further alterations to be made to the overall system. As the pressure controller utilised by the robot^[200] (Figure 4.2) was only capable of producing one source of pressure, the dispensing system needed to allow for both individual parts to be mixed using the same pressure source.



Figure 4.2: The JB1113 pressure controller^[197]

4.4.3 Programming the X Y Z Fisnar Deposition Robot

Programming of the deposition machine (Robot)s is simple with easy to follow instructions. Commands are followed and responses entered by a Teach Pendant. An LCD display prompts the user for a data input and once confirmed, automatically executes the next instruction. By this method a program can be executed quickly and simply.

4.4.3.1 X, Y, & Z Axis Movements

The robot's working area is 200 x 200 x 50 (X, Y, Z mm) which is adequate for testing the concept deposition system and a similar build volume to commonly used 3D printers (e.g. Objet30, MakerBot, etc.). The resolution of the robot is 0.01mm/axis which is pre-

cise enough to make objects with more than two times that of some 3D printers such as the Objet30 having a resolution 0.028 mm^[201].

4.5 Flow Characteristics of Individual Parts

To determine the dimensions of the deposition system, the flow characteristics of the two resins in the PU foam system were tested to regulate their individual volumetric flow rates. A simple test of the time taken for 1 ml of each resin to flow through nozzles of varying sizes was conducted to observe the effect of nozzle diameter on volume flow rate of the individual resins.

4.5.1 Instrumentation

A Fisnar JB1113N pressure controller, fed by a compressed air supply was used to supply pressure to the syringe barrel. A JB1113N foot pedal was used to manually dispense the liquids. 15cc dispensing barrels with Robot's straight cannula blunt end tips attached were used to give a controlled flow rate of the individual resins during experimentation. All tests were carried out within a fume cupboard to significantly reduce the risk of exposure of fumes out of making PU foams.

4.5.2 Methodology

The dispensing equipment was set up to allow for the manual dispensing of liquid via the use of the foot pedal controller connected to the pressure controller. 1 ml of the part being tested was squirted into a syringe barrel with a nozzle attached, secured to the airtight pressure source and dispensed into a plastic container. The time taken to dispense 1 ml was recorded using a stop watch. Each configuration was repeated 5 times which included tests of five different types of nozzles at a pressure of 1 bar for each of the two constituent parts totaling 50 tests. Experimentation of each part was performed using completely new syringes and nozzles to prevent cross contamination. The results obtained were plotted for comparison.

4.6 Modification of the Deposition System

Using the information obtained in the experimentation of flow characteristics of the individual parts, an estimation of the dimensions of two chambers in the bracket that would create a 50:50 compositions in the mixing nozzle was made. These dimensions then informed the design of the deposition system itself. Detailed requirements of the deposition system were listed based on investigations carried out on the PU foam components, the physical dimensions of the Deposition Robot, and the available manufacturing equipment on-site.

Requirements:

- Two fluid sources to nozzle
- Mixing chamber/nozzle
- Height of system within robot working area height of 50mm
- Able to be attached to the robot's front plate using M4/M5 bolts
- Solid enough to withstand pressures of at least 1 bar and weight of various attachments
- Wide enough to fit two syringe barrels which contain each part of PU foam
- Syringe barrels could be attached to Luer lock mechanism on deposition system
- Tight seal on components to prevent fluid leakage or pressure loss
- Two fluid chambers/pipes with varying internal diameters to produce 50:50 mixing ratio.

4.7.1 Mixing Chamber/Nozzle

Mixing nozzles similar to those used in two-part epoxy systems were investigated to determine their suitability for this application. As a small, precise nozzle was required, a MixTip mixing tip (Figure 4.3), the type used for making impressions of teeth in orthodontics was adopted as this was of a similar size to the syringes used with the Deposi-

tion robot, and fits well within the robot's operating range and also cheap and disposable.

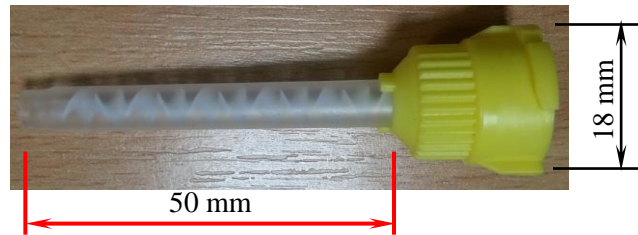


Figure 4.3: Two-part epoxy mixing nozzle for

4.7.2 Two Fluid Sources to Nozzle

The nozzle selected (Figure 4.4 'a') allowed for two fluids to be driven into the nozzle from the top and measurements of the two chambers were taken to determine the dimensions of the deposition system's chambers would need to ensure that connection could be made between the two using polymer tubing that would provide a tight seal on both.

Since the pressure controller supplied with the Deposition Robot only provided one pressure source, a small T-connector was attached to a section of hose as shown in Figure 4.4 'b' to split the pressure supply into two which would facilitate the use of two syringes in the deposition system.



(a) Isometric view of mixing nozzle with two tubes



(b) Two syringe barrels with visible T-section

Figure 4.4: Two fluid sources nozzle

4.7.3 Schematic Structure of X Y Z Deposition Machine

The vertical travel distance of the robot's front plate is 50mm (labelled in Figure 4.5 as 'Z Stroke'), which meant that for the deposition system to make full use of the robot's Z axis travel, it would need to fit to the front plate and extend to as close to 50 mm above the print bed as possible. With the distance from the front plate to the print bed being 139.5 mm, leaving room for a maximum height of around 90 mm for the entire deposition system before some of the Z travel distance would be unusable^[199].

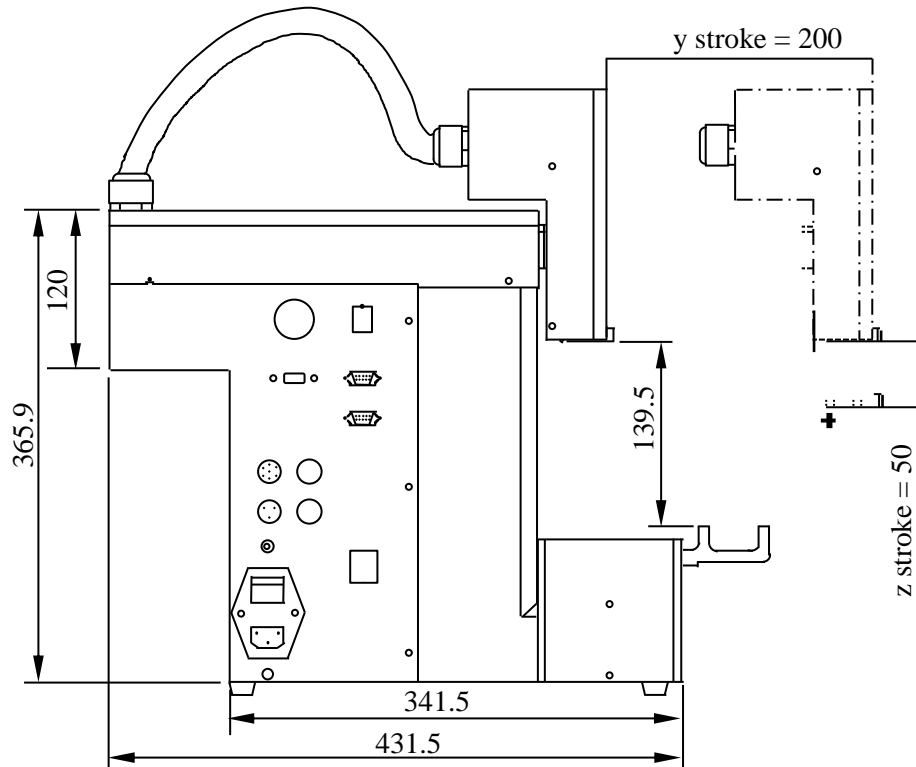


Figure 4.5: Schematic diagram of Deposition Robot's side view ^[196]

As the front plate of the robot has fittings for M4 and M5 bolts, the deposition system required holes to accommodate the bolts. Holes of 4 mm were added to the system to allow it to be fixed to the front plate and evenly spaced along the height of the system to give some flexibility to exactly where the system was fixed to utilise the largest working dimensions of the robot as possible (see Figure 4.6).

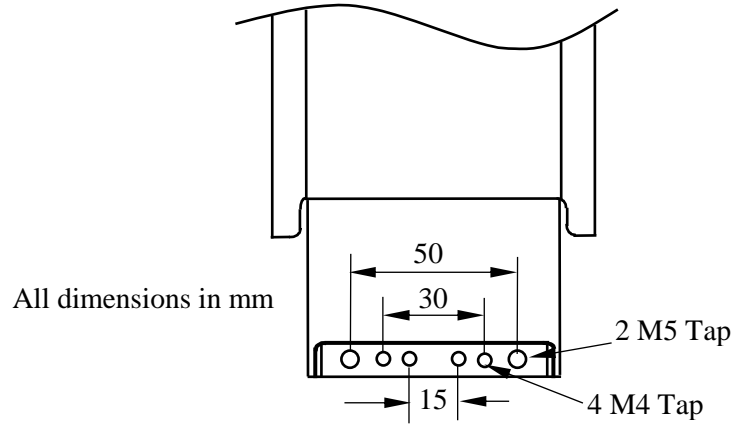


Figure 4.6: Fisnar F4200N front plate schematic diagram

4.8 Manufacturing of Parts for Modifying the X Y Z Deposition System

An Objet30 3D printer was used to print parts for the deposition system. The material used in the selected printer was the rigid, opaque, white material VeroWhitePlus (RGD835) which is strong enough to withstand the weight of two syringe barrels, the mixing nozzle, and the pressure inside, with an elastic modulus of 2-3 GPa and tensile strength of 50-65 MPa^[201] as the maximum pressure of the X, Y, Z deposition system used has a maximum 2.1 Mpa.

The deposition system needed to be wide enough to allow both syringe barrels to stand vertical and be easy to insert and remove with enough space for both barrels at all times. The minimum distance required between the two was measured to be 40 mm from the syringe barrel nozzles due to the green locking mechanism on top of the syringes (Figure 4.6) being approximately 30 mm wide. As a result, the two chambers on the deposition system were placed 50 mm apart.

4.8.1 Syringe Barrels Attachment to Luer Lock Mechanism on the Deposition System

The Fisnar syringe barrels have a locking mechanism at their tips known as a Luer lock mechanism shown in Figure 4.7. This is a screw threaded of a specific size dictated by ISO

standard 14972:1998 by Lee-Liacer, Jason and as such, the dispensing system required these fixings to allow the syringe barrels to fit to the dispensing system with an airtight seal and secure fit.



Figure 4.7: Fisnar 3cc syringe barrel with visible Luer lock

With the Luer lock fittings on the deposition system, a pipe was required to allow the individual parts to flow from the syringe barrels into the mixing nozzle. This was designed with a different internal diameter on each side to ensure a 50:50 mixing ratio of the two parts, once they arrived at the mixing nozzle.

4.9 Final Modification on the X Y Z Deposition System

The final design of the deposition system incorporated all the listed design requirements and an initial prototype was made to check fittings and tolerances. Once these had been assessed and it looked good, a final deposition system was manufactured to be used in final testing.

4.9.1 Overall Structure of the 3D Printed Bracket

The printed bracket is geometrically simple with the only complex parts being the Luer lock fittings on top and the tubes through which the resins flow (Figure 4.8). The bracket was designed with three vertical rectangular slots to reduce the cost of material without compromising its strength. The diameter of each tube is approximately three times the diameter of the largest inner tube to be strong enough to handle regular usage and is shaped with wide elbows to provide a smooth fluid flow and avoid structural weakness.

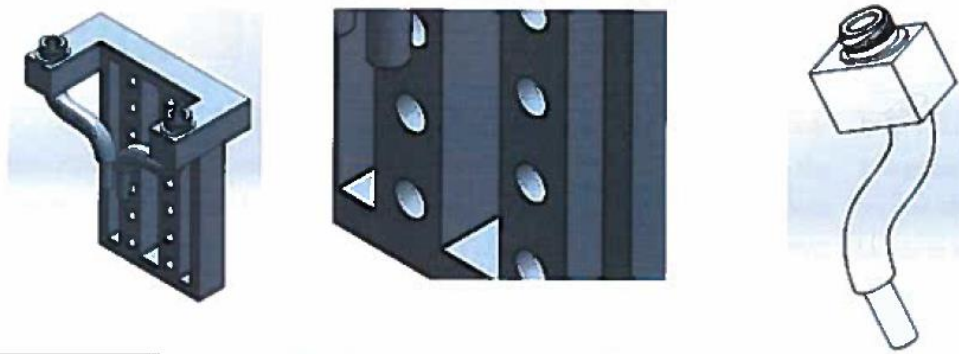


Figure 4.8: Overall structure of the printed bracket attachment

4.9.2 Fixtures and Fittings of the Bracket

The bracket consists of two symmetrical tube sections which contain the resins (polyol and diisocyanate) separately and be directed to the mixing nozzle at different rates as the inner diameter of the right-most tube is slightly smaller. The reduced sections were 4 mm diameter to allow the use of 4 mm standard pipe hose to connect the mixing nozzle to the bracket. Holes of 4 mm in diameter and 15 mm apart were placed at even intervals on the bracket to allow it to be fixed to the front plate of the robot with M4 screws. The two 4 mm tube sections to which the mixing nozzle is attached are placed 7mm apart which is the distance between the two tubes of the mixing nozzle to ensure that the nozzle fit easily. The mixing nozzle is attached to the two tube sections using small PVC hose of the same internal diameter as the external diameter of the two reduced tube sections on the bracket. Two Luer lock fitting on top of the bracket allow syringe barrels to be attached with an air-tight seal. The entire fixtures and fittings are shown in Figure 4.9.

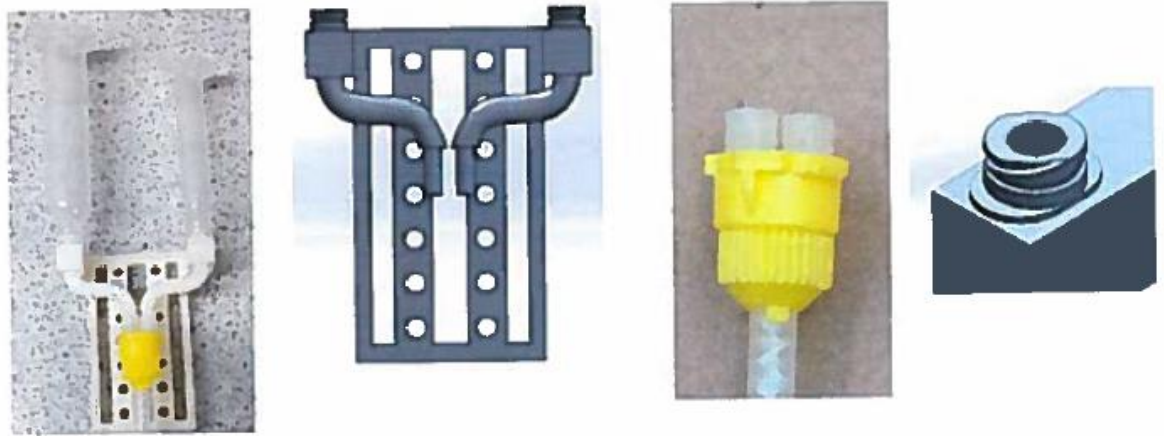


Figure 4.9: Fixtures and fittings of bracket

4.10 Testing of the Modified X Y Z Deposition System

4.10.1 Flow Rate & Gauge Pressure

Initially, the deposition system was tested without attaching it to the front plate of the robot in a similar fashion to the initial flow rate testing of the individual parts to examine the rate at which both syringes emptied to ensure an even mix at the mixing nozzle. Figure 4.10 shows the deposition system with attached mixing nozzle and syringe barrel.



Figure 4.10: The deposition system with attached mixing nozzle and syringe barrel

Using the prototype deposition system, foam was manually dispensed using the pressure controller foot pedal. The 3 cc syringe was filled with 3ml of part B resin, and the 15cc syringe barrel filled with 3 ml of part A resin. The pressure controller gauge was initially set at 1 bar.

After three repeated tests, it was established that a 50:50 mixing ratio had not been achieved due to only one chamber emptying at a time, though there were drips coming from the other. This initial test allowed for closer observation of the way pressure was distributed throughout the two barrels and it was realized that only one barrel was fully pressurised.

A second test was performed at 2 bar pressure and a good mixing ratio was achieved as both chambers of resins were emptying at the same time.

The flow rate of the PU mixture from the mixing nozzle however, was too great to allow for use in the printer due to the wide diameter of the mixing tip. As a result, a small Fisher Brand SureOne pipette tip was attached to the mixing nozzle using superglue. The pipette nozzle tip had an exit diameter of 1mm which greatly reduced the flow rate to allow for observation of printed tracks using the deposition robot. Figure 4.11 shows the test rig setup in its entirety with the bracket fixed to the front plate of the deposition robot.



Figure 4.11: Test-rig with visible teach pendant setup

4.10.2 Creation of Tensile Test Specimens Using X Y Z Deposition Robot

Using the prototype deposition system, foam was manually dispensed using the pressure controller foot pedal. Two 30 cc syringe barrels were filled with 30 ml of resin, one syringe with part A and the other with part B. The gauge pressure of the pressure controller was set to 2 bar and layers of PU foam were built up inside a plastic container by activating the foot pedal to dispense mixed PU in liquid state and waiting for it to foam and then applying another layer on top of it.

In each case, enough mixture was deposited to cover the entire base of the container with the smallest amount of liquid before foaming, at which point it rose to around 15mm and was allowed for approximately 5 minutes to complete foaming/curing. Layers were added until cured foam of around 50mm depth was created in the container.

Once this rectangular shaped layered foam was fully cured, the same cutting and machining process as in the previous chapter was used to create the specimens that could be tested for tensile strength.

4.11 Proof of Concept Test

Once the flow of the material was brought under control using the small pipette nozzles, the deposition system could be tested while attached to the front plate of the robot.

3ml of each of the resins was drawn into the separate syringe barrels of the deposition system and attached to the bracket which had been fixed to the front plate of the deposition robot (see Figure 4.10).

The dispensing robot was programmed with commands using the hand-held Teach Pendant. The program instructed the robot to print 5 tracks parallel to each other with uniform length and pressure, and a set distance of 10 mm apart to ensure that two laid strips do not touch each other after curing. The syringe barrels were filled with equal amount of resin and attached to the front plate securely with all seals intact, the deposition program was run.

The program was run through and the robot deposited the contents of the two syringe barrels to the Perspex surface on the bed beneath. After the program had finished, the

resulting tracks were allowed to fully cure and the bracket, mixing chamber and syringe barrels removed.

The widths and heights of the tracks printed were measured for comparisons.

4.12 Discussion of Results

4.12.1 Flow Characteristics of Individual Parts

Figure 4.12 illustrates the volume flow rate of the two parts of PU foam (polyol and diisocyanate) system and the effect of nozzle diameter on the flow rates. The two nozzle diameters that gave flow rates of 0.1 ml/s (approximately 1.0 mm for part A and 0.8 mm for part B) were selected for the final design of the bracket used to deposit the PU foam.

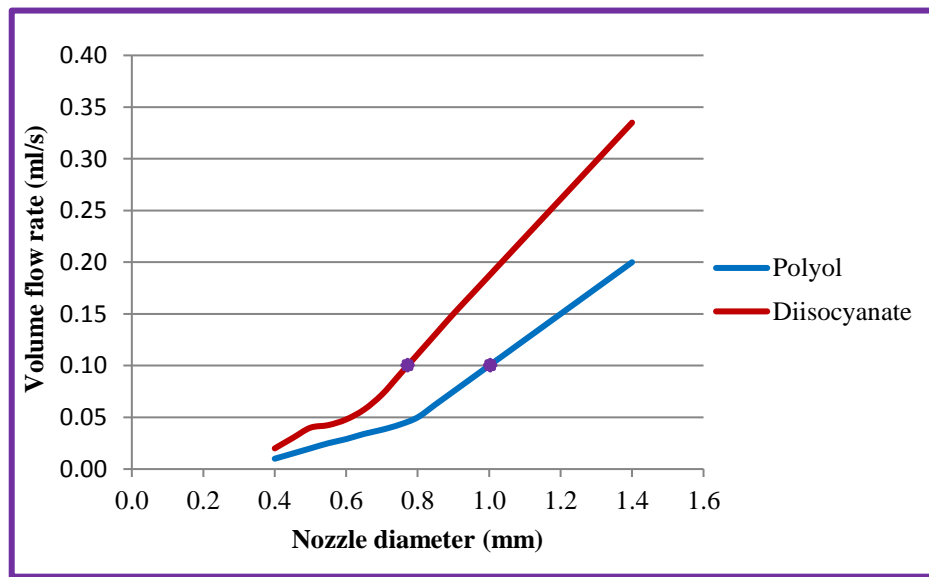


Figure 4.12: Flow characteristics of polyol and diisocyanate

4.13 Evaluation of the X Y Z Deposition Robot

4.13.1 Tensile Test Results of Specimen Created by Deposition Method

The Table 4.1 illustrates the brief summary of the results obtained from the analysis of the characteristics of the PU foam produced by the hand controlled deposition method using the deposition robot.

Figure 4.13 shows the tensile test results of the specimens that were created using the deposition system held in hand with the mixing ratio being approximately 50:50. The tensile tests were conducted under the same conditions as used for the specimens cut from the foams produced using the conventional method of mixing and casting in mould. The results obtained from the hand held deposition method were found to be within the ranges of the ones produced using the conventional method for the restricted foaming direction. The tensile strengths for the specimens are illustrated in Figure 4.14 with the highest being approximately 323 kPa with a corresponding strain of 0.231 whilst the minimum strength was approximately 290 kPa with a strain of 0.220. The various strengths and their respective strains are shown in Table 4.1.

Table 4.1: Summary of PU foam characteristics by hand-held deposition method

Sample	1	2	3	4	5	Average	STDEV
Tensile Strength (kPa)	293.0	290.2	310.4	322.9	299.0	303.1	13.5
Strain (ϵ)	0.175	0.220	0.287	0.231	0.099	0.202	0.070

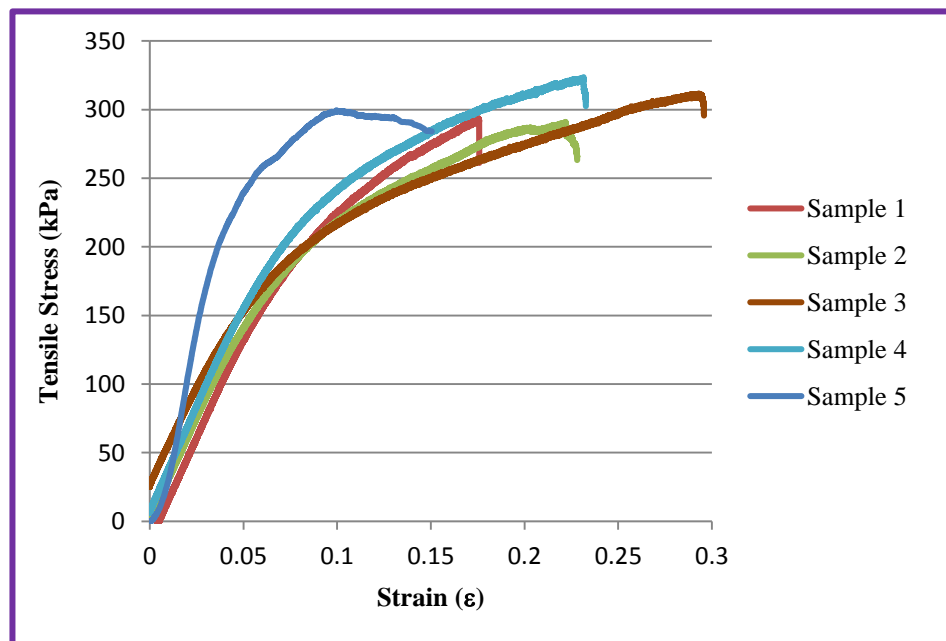


Figure 4.13: Stress versus strain curves for samples made using the deposition system

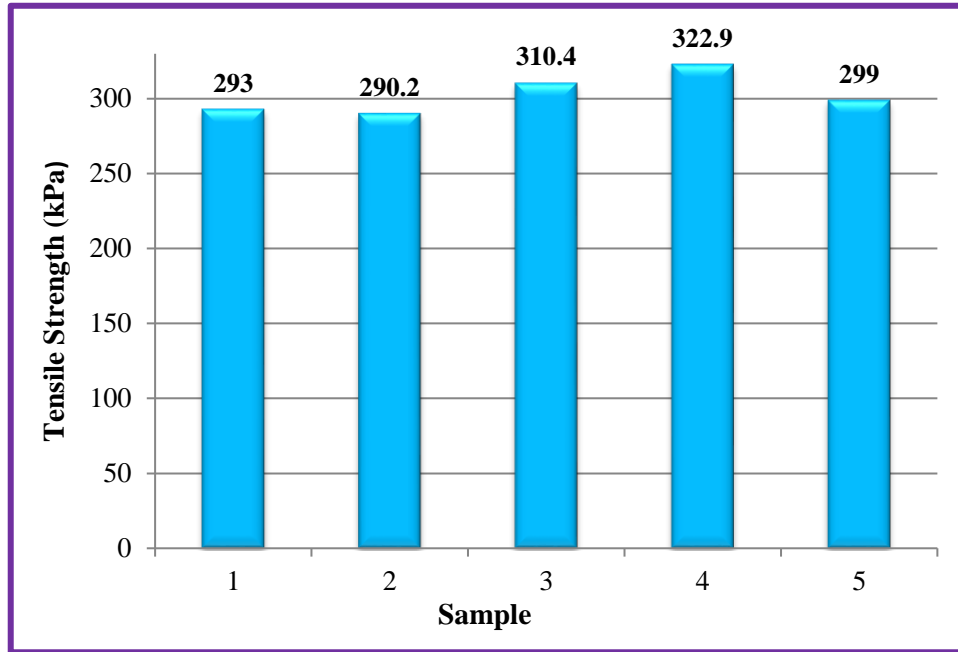
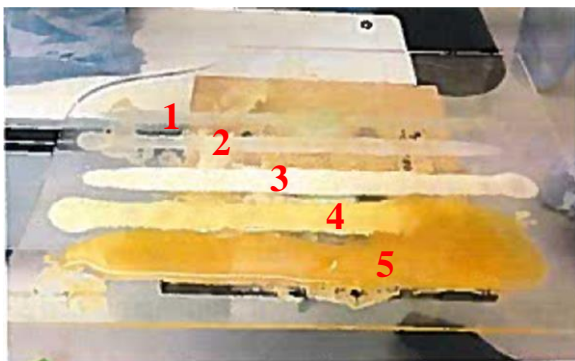


Figure 4.14: Tensile strengths of foam samples produced by deposition system

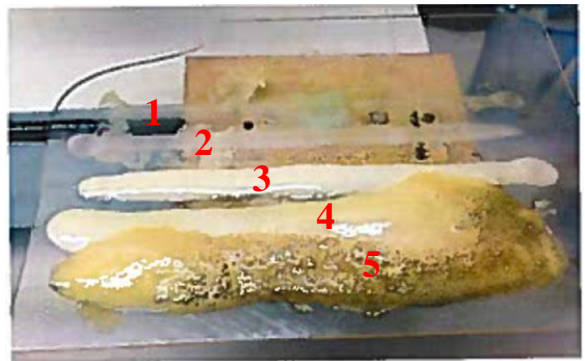
4.13.2 Proof of Concept test –Printed Tracks

Printed Tracks

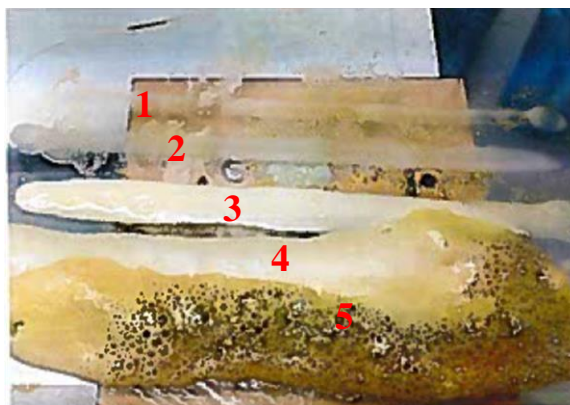
With the brackets attached to the deposition robot, the robot was programmed and used to automatically print five tracks. The width of each track was measured in five locations equally spaced where clear definitions of the width of the track were visible and the average taken. The results are as shown in Figure 4.15 and the Table 4.2 illustrates tracked foam sizes after curing.



Stage 1: Tracks immediately after printing



Stage 2: Two minutes after printing



Stage 3: 10 minutes after printing

Figure 4.15: PU foam tracks printed by the programmed Fisnar 4200N

Table 4.2: Measurements of cured printed tracks of PU foam

Track	Average Height (mm)	Average Width (mm)
1	29.01	7.83
2	24.04	2.313
3	13.50	0.90
4	9.24	0.20
5	7.87	<0.10

4.14 Evaluation of the Deposition Method

4.14.1 Meeting of Initial Requirements

Reference to the requirements for deposition system as outlined in sub-section 4.3.1, an overview of the characteristics for the system were listed which informed an improved system design.

4.14.1.1 *System Allowed the Use of Liquids*

The system included two Luer locks located at the top of the bracket to which syringe barrels of liquid could be attached. The liquids were then driven through the system using pressurised air when in operation. This allowed pre-measured amount of liquid to be loaded into the indi-

vidual syringe barrels attached to the bracket of the deposition system and driven through a closed system so the deposition system fulfilling this requirement.

4.14.1.2 System Used Disposable Components at Wherever there was Contact with the Combined Mixture

The bracket fed the two PU resins into a mixing chamber which could be removed and disposed of; once each printing task was completed. Both the mixing chamber and attached pipette could be considered disposable and cheap enough to replace after each print job.

4.14.1.3 The Two Individual Parts Mixed Uniformly

The mixing chamber attached to the bracket enabled the two liquids sources to be driven through the chamber, combined, and deposited as one mixture.

4.14.1.4 Programmable Control

The X, Y, Z deposition robot features a hand-held Teach Pendant that could be used to issue commands to the robot to print simple shapes such as lines or curves. Because of this, the simple test of printing tracks and having it be automated was possible.

4.14.1.5 X, Y, and Z Axis Movement

The X, Y, Z deposition system features a build volume of 200mm x 200mm x 50mm (X Y Z) which was adequate for a proof of concept test.

4.14.2 Issues Associated with the Deposition System

4.14.2.1 Mixing Ratio

Throughout the testing, it was observed that the deposition system could not reliably mix both resins at the desired 50:50 mixing ratio. This is highlighted in the proof of concept test (Figure 4.15) in which 5 tracks deposited were clearly of visibly different mixing ratios of component parts. This may be attributed to the single pressure source to both syringe barrels which meant

the dimensions of the sections of the bracket needed to be designed with different diameters to compensate.

For the system to produce the desired mixing ratio more reliably, individual pressure source would be required for each syringe barrel and, or an internal stirrer allowing fine-tuning of the system on the fly.

4.14.2.2 Seals Around Disposable Mixing Nozzle

The seals around the 4 mm PVC hose which connected the bracket to the mixing nozzle were not completely air-tight; as a result, a small amount of superglue needed to be applied to the PVC hose to completely seal any gap.

This did not solve the problem but as a result, once testing was completed, removing the mixing nozzle from the bracket required the use of a scalpel and small amount of force to scrape away hardened superglue left behind. This affect the long-term usability of the bracket as the continued application of force to the bracket would cause damage after number of use.

4.14.2.3 Capacity of Syringe Barrels

The system is limited by the size of syringe barrels attached to the bracket because the amount of material that can be used in the system is dependent on their maximum capacity, in this case around 110 ml from two 55 cc syringe barrels which are the largest syringe barrels produced by the manufacturer.

4.14.3 Issues Associated with the Proposed PU Deposition System in Relation with Additive Manufacturing

4.14.3.1 Foaming / Curing Time

The foaming/curing time of PU foam means that for one layer to be built on top of another, the foaming must complete and cure to some extent to provide a solid support on top of which the next layer is built. This potential slow build time highlights a major issue with the use of PU foams as a material for use in AM technology. Hence, further investigation into ways of speed-

ing up the process of foaming and curing would be necessary such as partially addressed in chapter 3 by pre-heating of the resins and further in future research.

4.14.3.2 Flow of Mixture

When the PU foam mixture first leaves the mixing chamber it continues to flow. As a result, the PU foam “cream” will spread outward until there is uniformity in the depth of the liquid. This will have a significant effect on the accuracy of any object being built as the layer thickness would be dictated by the thickness at which the cream mixture settled before foaming.

4.14.3.3 Size and Shape Difference after Foaming

As mentioned earlier, the PU foam components (resins) together foams to over 20 times of the initial volume of both parts and other additives are combined. As a result, the material’s final foamed shape by comparison to the shape of the mixture before foaming varies enormously which means that the exact change in shape of the material after foaming would need to be identified so that it could be compensated for when building a structure.

4.14.3.4 General Observation of the X Y Z Deposition System

Due to the uncontrollable flow mixing, expansion and curing as discussed in this section, the author concluded that an alternative method was required.

CHAPTER FIVE

DESIGN OF IN-FLIGHT MIXING SYSTEM USING AIR-BRUSHES

5.1 Introduction

Traditionally, the base materials of PU are continuously stirred either by mechanical or electronic means to obtain a homogeneous mixture. The homogeneous mixture is then cast in a mould and cut to the required shape and size for its intended use after it has fully cured. The failure of the modified X Y Z deposition machine to produce a homogeneous foam and also, the discarding of the nozzle used after each cycle did not match the traditional method of building the material. This could not further be developed to be used as an Additive Manufacturing process for building PU foam, hence, leading to the design of a system that will avoid the reactants coming into contact in a chamber but outside and will uniformly mix to produce a homogeneous foam. Hence, the proposed in-flight mixing system which will bring together the PU resins under pressure as sub-nanolitre droplets, acting as internal wall-less micro-reactors.

5.2 Methodology for the In-flight Mixing Using Airbrushes

The design of the proposed system is derived from various factors from both the literature reviewed and various experimental results. Since the final design will be in the family of Additive Manufacturing technology, its working principle should be carefully designed to satisfy the requirements of the technology. Therefore, the results obtained from the PU foam characteristics in chapter 3 as well as the proof of concept using X Y Z Deposition system in chapter 4 were critically studied. Even though a concept was proofed by dispensing PU on a surface using the X Y Z Deposition, the full requirements to obtain uniform PU foam for the intended purpose was not met. The issue of changing the mixer and the nozzle unit refutes the essence of Additive Manufacturing due to non-continuous flow of material dispensing to build a product. Based on the information gathered, the decision was taken to design a system which could continuously

dispense PU foam uniformly mixed outside a mixing chamber to meet the requirements of AM and a final product that will satisfy the purpose of medical scaffolds.

5.3 Design Requirements of the In-flight Mixing System

One of the key factors to consider for many additive manufacturing applications is an understanding of the way the materials are built up three-dimensionally. It is therefore important to study how the successive layers of material perform as they are deposited on previously deposited layers. Other factors such as the feature sizes, surface spreading, and related properties are important issues to keep in mind^[26]. As regards the aim of this research, the synthesis of polyurethane-based materials has been used as particular illustrative example as is extensively dealt with in chapter three. The chemistry of polyurethane involves the preparation of two separate resins, one of the resins containing polyol and the other containing diisocyanate. In this design, the two resins were to be sprayed separately at the same time and allowed to react to form urethane bonds. This is to address the issues of overcoming the production difficulties of PU deposition system to suit its dispensing using Additive Manufacturing technology and also produce foams of different mixing ratios within the same part. The inclusion of additives to vary certain desired properties of the foam may require a third reservoir with its nozzle which would be on and off as needed or earlier mixing with any of the resins before dispensing if there would not be a chemical reaction. Or, if a support material would be required then there should definitely be a third nozzle. The following requirements were set to achieve the aim:

- 1) There must be two or more reservoirs which will form part of the entire system to carry the two main resins and possibly an additive material separately.
- 2) There should be sub-system that will provide constant, elevated temperature to pre-heat the main resins of PU in their individual reservoirs to maintain low viscosity.
- 3) There must be a pressurised air system linked to the dispensing nozzle to draw the resins and dispense them under compressed air pressure.
- 4) The individual resin nozzle orifices should be adjustable to control the flow of resin to the mixing point.

- 5) There should be a constant supply of heat to follow close to the dispensed mixed resins to increase the rate of foaming/curing.
- 6) A third nozzle would be required to print a support structure.

5.3.1 Pre-heated sub-system

The viscous nature of the PU foam resins makes them difficult to easily flow, especially through a small diameter tube, orifice, or nozzle. Previous tests conducted (as in chapter 3 section 3.3.7) indicated that when the viscosities of both the polyol and diisocyanate decrease by heating, they flow easily through a nozzle of diameter as small as 0.5mm or even less with pressure or gravitational force and also, easily mix uniformly with few mixing turns. From the previous experimental results, a pre-heated temperature up to 60°C has very little effect on the physical properties of the material as the temperature of the mixture at 50:50 mixing ratio during reaction rises up to about 54°C when mixed at room temperature (approximately 20°C). It was also established that pre-heating the resins separately before mixing them and other additives (if required) foams and cures with far less time compared to ones mixed at room temperature.

5.3.2 Pressurised Air System Linked to the Nozzle of the Resin

Based on the requirements set in section 5.3, the airbrush which was an available on-site equipment that met most of the requirements was modified to meet the criteria. The pressurised air system (Figure 5.1) linked to a bottle to draw resin was based on the principles of airbrushes. The airbrush is a small, air-operated tool that sprays various fluid including ink and dye; usually paint using the process of nebulization.



Figure 5.1: Airbrush system^[201]

5.3.3 Classification of Airbrushes

Airbrushes are usually classified based on three characteristics, namely; the action performed by the user to trigger the flow of the paint or fluid, the mechanism used to feed the fluid to the airbrush, and the point at which the paint and air mix^[202].

5.3.4 Selection of Airbrushes Needle Size

Airbrush needles vary in sizes depending on the amount of flow needed. The most important aspect of buying airbrush needles involves selecting the right size needle and nozzle. Both the needle and nozzle come as a similarly-sized set. Manufacturers mostly express needle size by diameter in mm. Also, terms such as medium, fine, and ultra-fine may be used to describe the needle detail. The following chart (Table 5.1) depicts the various airbrush needle sizes, with brief description of their applications^[203].

Table 5.1: Table of Airbrush needle description and uses^[202]

Needle Size (orifice)	Description
0.4 mm to 0.6 mm	Largest size to consider For general purpose airbrushes Most popular type of needle Only suitable for base coating
0.3 mm to 0.35 mm	High-end of detailing range of needles Suitable for some freehand that does not require fine lines

Needle Size (orifice)	Description
0.2 mm to 0.25 mm	Base coating takes longer than larger needles Fine spray patterns Perfect for more advanced artists
0.15 mm and smaller	The best spray pattern details Not recommended for base coating Most expensive type of airbrushing needles

5.3.5 Principle of Operation of Airbrush

When a fast gas stream is injected into the atmosphere and across the top of the vertical tube (see Figure 5.2), it is forced to follow a curved path up, over and downward on the other side of the tube. A lower pressure is created on the inside of the curve at the top of the tube by the curved path. The curve causes lower pressure near the tube and the atmospheric pressure further up is the net force causing the curved, velocity -changed path which is called radial acceleration. This is explained using the Bernoulli's equation.

The difference between the reduced pressure at the top of the tube and the higher atmospheric pressure inside the bottle pushes the liquid from the reservoir up the tube and into the moving stream of air where it is broken up into small droplets (not atoms as the name suggests) and carried away with the stream of air^[202].

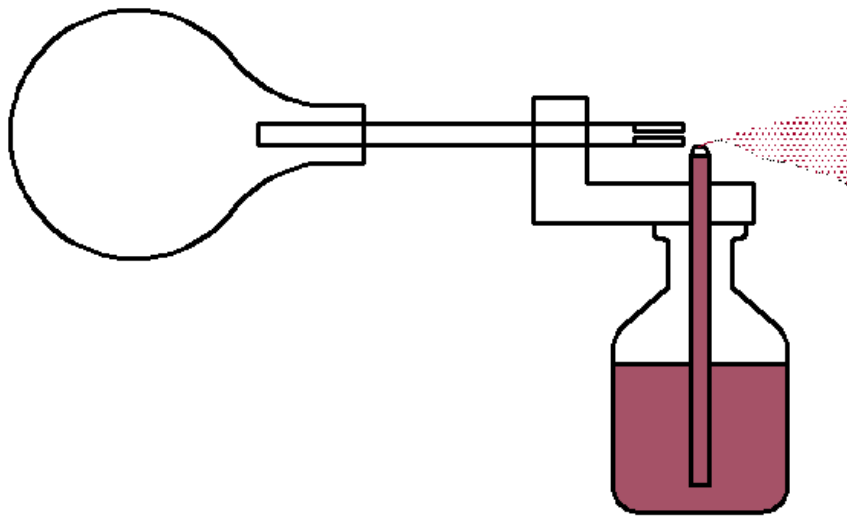


Figure 5.2: Principle of atomizer^[201]

Figure 5.2 shows the principle of an atomizer where the air jet coming out of the horizontal cane causes a depression on the vertical tube drawing liquid from the small bottle and dispensing it in tiny drops.

5.3.5.1 Mix Point of Airbrush

Airbrushes mix point could be either internal mix or external mix. The internal mix has the fluid to be sprayed and the air mixing inside the airbrush (in the tip) creating a finer atomized mist of fluid. The external mix has the air and the fluid exiting the airbrush before mixing with each other, which creates a larger coarser atomization pattern. The latter is less expensive and more suitable for covering larger areas with more viscous fluid.

5.3.5.2 Flow Adjustment of Fluid at Mix Point – Variation of Mixing Ratio

The upward and downward movement of the nozzle adjusts the distance between the tip of the nozzle and the mid-stream of the compressed air (Figure 5.3), thereby increasing or decreasing the amount of fluid to be drawn. These adjustments will allow the supply of resins to be varied as they are supplied from different chambers at different times in the same cycle.

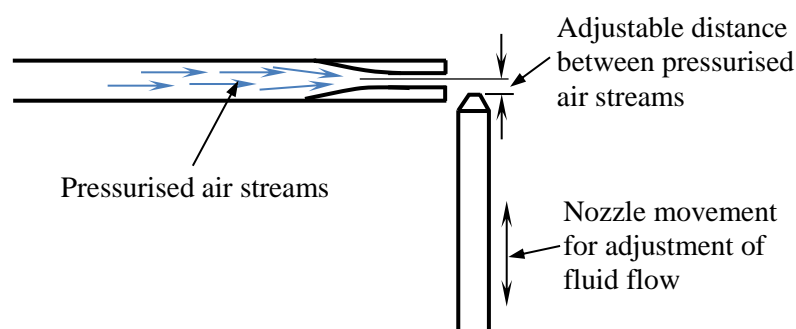


Figure 5.3: Flow adjustment of fluid at mix point

5.3.5.3 Constant Supply of Heat

The previous analysis in chapter 3 (Characteristics of PU foam) indicated that at high temperature, the foaming time is significantly reduced and therefore decreasing the curing time. To improve the efficiency of the system, the resins after pre-heated before passing through the nozzle should also be kept at an elevated temperature to reduce the foaming and curing time. A constant supply of heat directed to the dispensed foam will therefore be necessary.

5.3.6 Support Material Nozzle

Since the nature of PU foam base materials are in liquid form, there would be the need for a surface which has enough strength to hold them in their liquid or semi-liquid state. Also, before foaming is completed and fully cured, it is soft in nature therefore, a third nozzle is required to print a support material to support overhang parts.

5.4 Equipment Used for the Spraying – Humbrol Airbrush

On-site equipment adopted for the proof of concept of the in-flight mixing of PU foam and dispensing were two Humbrol airbrushes (Figure 5.4)^[204] that contained the PU resins separately.



Figure 5.4: Humbrol Airbrushes ^[203]

5.4.1 Design Criteria

The two airbrushes were to be designed to meet certain criterion to satisfy the intended purpose. The following were therefore set to be met:

1. Be able to hold the two nozzles in position at a required distance apart.
2. Be able to hold the two nozzles in position at an adjusted angle.
3. Parts of the holder should be as small and light in weight as possible and durable.
4. The holder should be easy to be adjusted and use.

5.4.2 Design of a Holder

The holder was therefore designed in two pieces using Solidworks software with individual small parts printed using MakerBot Replicator printer with PLA plastic and assembled together. The airbrushes were to be held in their positions at distances and angles using 3MM bolts and nuts (Figure 5.5).

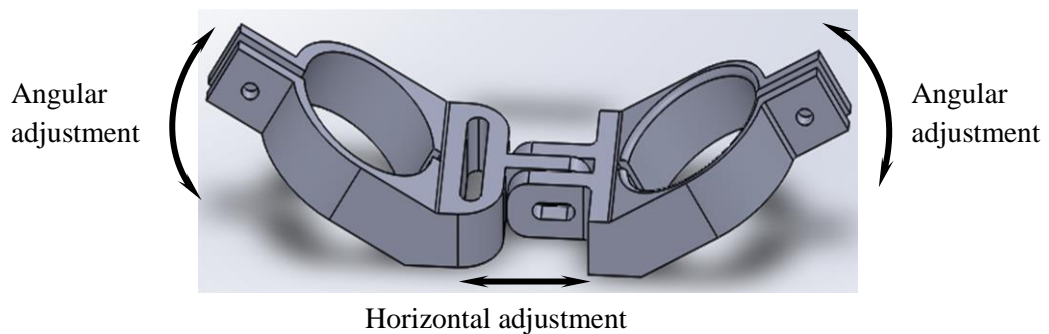


Figure 5.5: Adjustable holder for keeping airbrushes at distances and angles

5.4.3 Compressed Air Supply

The available on-site equipment used to supply compressed air was a portable TC2000 compressor. This supplies air up to a pressure of 5 bar. For the airbrushes to supply fluid under the same pressure, it meant that the compressed air supplies must be controlled to ensure that equal amount of compressed air is delivered to the individual airbrushes. Since the compressed air supplied by the compressor was from only one source, a system was required to distribute the air to the two airbrushes at the same pressure. Therefore, a T-connector was designed with the same T-arm dimensions to ensure that the same amount of compressed air was supplied to the airbrushes as shown in Figure 5.6.



Figure 5.6: T-connector distributing compressed air to the two nozzles

5.4.4 Flow Rate Comparison

The two air brush bottles were filled with their respective resins (polyol and diisocyanate) to a height of 30 mm and heated to 20°C, 30°C, 40°C, 50°C, and 60°C to compare the flow rate of the two resins at full opening of the airbrush valves and at various temperatures stated. The pressure of the TC2000 air compressor was set at 1 bar and ensured that there were no air leakages. The polyol in its bottle was heated from 20°C to 60°C at intervals of 10°C. With the compressor on and the valve fully opened, the time taken for the resin to drop a height of 5mm was recorded. This was repeated for the diisocyanate and the results of the two resins were tabulated as shown in Table 5.2.

Table 5.2: Flow rate comparison of polyol and diisocyanate

Temperature (°C)	Time (seconds)	
	Polyol	Diisocyanate
20	423	385
30	313	313
40	251	251
50	227	227
60	227	227

From the results obtained, the flow rate at 40°C for both the polyol and the diisocyanate were almost the same. As well, the time for 50°C and 60°C to drop a height of 5 mm were the same and also, the same for both the polyol and diisocyanate. This indicates that at 40°C and above the viscosity of both the polyol and the diisocyanate are almost the same. The author therefore agreed to use 40°C as the pre-heat temperature for the proof of concept but be heated 5°C above to compensate for heat loss depending on the environment temperature.

5.4.5 Pressure Selection for the Resins Flow

With the T-connector firmly secured in the pressure outlet of the compressor, the two airbrush bottles were filled to 30mm full and pre-heated to 45°C. The pressure of the air compressor was set at 1bar and the two airbrushes were opened at the same time at full throttle to compare their flow. It was realised that at the pressure of 1 bar, the flow was not continuous and uniform, indicating that the pressure was not enough to operate the two airbrushes at the same time. The pressure was increased to 1.5 bar and the test repeated. It was realised that with the 1.5 bar compressor pressure, the flow at full throttle was uniform for the two airbrushes.

5.4.6 Variation of Product Width

Variation of the width of foam produced is dependent on how far apart nozzles of the two airbrushes are; as it increases with increasing distance and the angle between them (Figure 5.7).

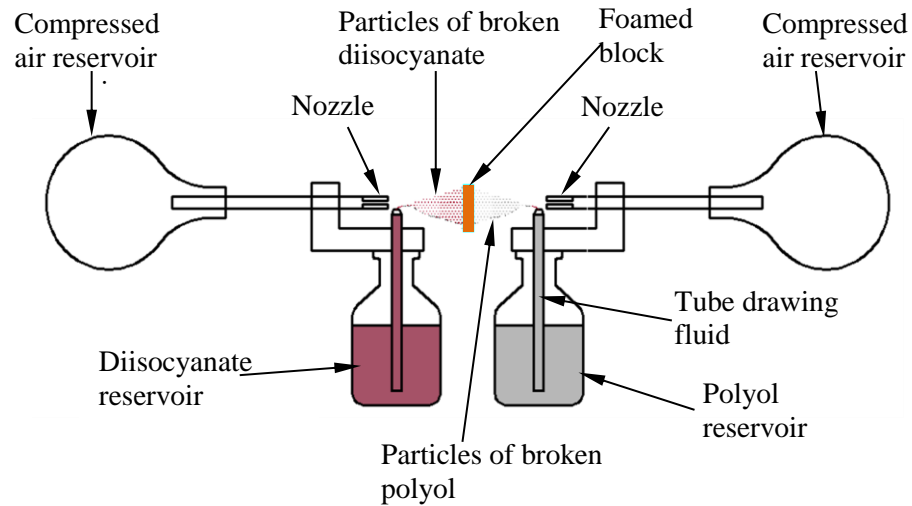


Figure 5.7: Foam width variation diagram

5.5 Testing of the In-flight Deposition System

The test rig was set up in a spray booth (Figure 5.8) to ensure that any possible fumes would be extracted. The pressure of the air compressor was set at 1.5 bar and the two airbrush bottles were filled with resins (polyol in one bottle and diisocyanate in the other) to 30 mm and heated to a temperature of 45°C using the Carbolite oven. The airbrushes were quickly held in the holder at an angle of approximately 30° between the two airbrushes by adjusting the built airbrushes holder. The compressor was switched on and the brushes were moved steadily with the brushes nozzles directed to the surface of deposition to dispense the two resins together in sub-nanolitre droplets to converge on the surface for four rows. The time taken for each dispensed mixture (substrate) to start foaming was recorded for comparison.



Figure 5.8: Test rig for the in-flight mixed deposition

5.5.1 After-heating of Dispensed Resins

The process was repeated to print another four row substrate which the nozzles were followed steadily by an electric hand-held heater (Figure 5.9) to heat the dispensed substrate in the same direction as the nozzle movements. The results obtained were recorded and compared to the results of the dispensing without after heating.



Figure 5.9: In-flight mixed dispensing with electric air heater

5.5.2 Determination of Skin Effect on Previous Layer

This test was conducted to check whether there is skin effect of one layer atop previous cured layered foam. The method used above was employed in laying on a surface and allowed to fully cure for about five minutes. The spraying was repeated to spread another layer on top of the cured one. This was also allowed to cure and a cross-section of the layers was cut and viewed using the Alicona scanner.

5.6 Discussion of Results

From the tests conducted, the time taken for the dispensed substrate to start foaming was 26 seconds. The time taken for the first laid substrate to completely foam was recorded as approximately 2 minutes 35 seconds. The time taken for the laid substrates to start foaming as the heater was immediately directed to follow the substrate was 18 seconds and the time taken to complete foaming was 56 seconds. Comparing the two scenarios, the time taken for the substrate to start foaming and was observed that foam-ing/curing have improved to a reasonable degree. The foam produced after curing using the pre-heated and after heated system is shown in Figure 5.10.

From the measurements the widths of the foams produced were varied with the maximum being 9 mm and the minimum being 6 mm. The depths measured were not uniform varying from 1.4 mm to 2.3 mm at different points on the foam.

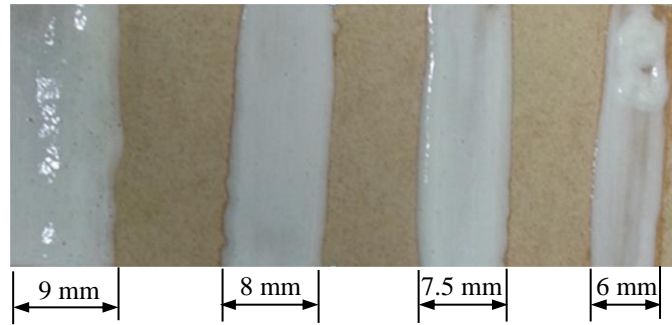


Figure 5.10: Patterns produced using airbrushes

5.7 Skin Effect of Two Layers of PU

Figure 5.11 shows the cross-section of the two different layers by visual inspection.

By visual inspection, even though the two layers could be differentiated, it was seen to be bonded and could not be separated at the joint. A further inspection was made by using the Alicona scanner to analyse the condition between the first and second layers. The image obtained by the Alicona scanner is as shown in Figure 5.12.



Figure 5.11: Two layered foam

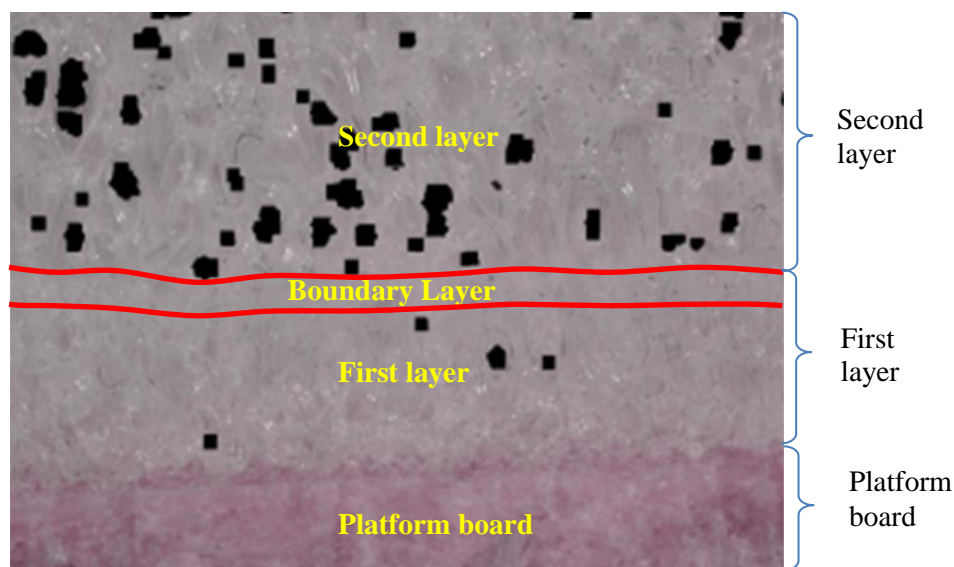


Figure 5.12: Boundary layers captured using Alicona scanner

From the Figure, even though it was difficult to separate the build platform and between the first and second layers, it was observed that there is clear distinction between the build platform and the first layer as the platform had different colour. It was also observed that the structure of the first layer becomes denser as it gets to the top (boundary between the first and second layers) and very dense at the region bounded by two curves.

It could therefore be said that even though there was strong bonding between two layers of PU foam, the skin layer between them is very dense.

5.8 Effects of Dispensing Delays

This test was conducted by the airbrush system to determine the effects of delay of movement of dispensing unit. The two resins were heated in their respective airbrush bottles to a temperature of 45°C. The compressor was set at 1.5 bar and with the designed airbrushes holder adjusted at an angle of 30°, the airbrushes were held at a distance of approximately 10 mm from a surface to direct the heated resins to the same point for period of 40 seconds. This was repeated for a period of 30 seconds, and 20 seconds respectively. After dispensing each image on the substrate it was immediately followed by a heater to enhance foaming/ curing time as previous. The foams created are shown in Figure 5.13.

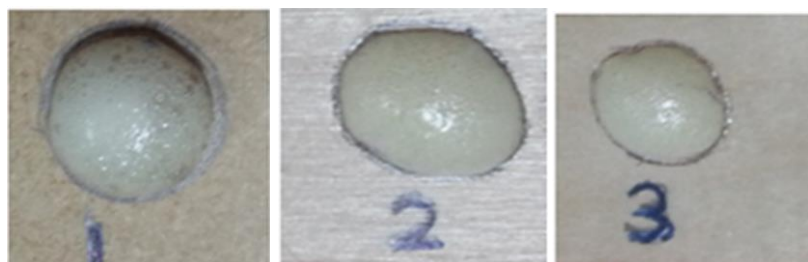


Figure 5.13: PU images produced by holding the nozzles at one position

The images obtained could be likened to an oblate ellipsoid but were not uniform in diameter; therefore, diameters were taken at three different places and their average and heights as recorded by the Alicona scanner were used to calculate their respective volumes as illustrated in Table 5.3.

Table 5.3: Image sizes due to dispensing delays

Delay Period (sec)	Average Radius (mm)	Average Height (mm)	Average Volume (mm³)
40	5.52	5.35	217.09
30	5.23	4.94	179.82
20	4.27	4.23	102.83

5.9 Evaluation of the In-flight Mixing Deposition Method

5.9.1 Meeting of Initial Requirements – Proof of Concept

- System had two reservoirs with each containing one part of the PU resins separately
- Even though there was not a constant supply of heat as part of the system, an oven was used to pre-heat the resins and electric hand control hot air blower was used to post-heat the resins after deposition.
- The airbrushes linked with a pressurised air supplied by TC 2000 compressor which was able to draw the resins and dispense them under compressed air

- The control of the built adjustable holder made it possible to adjust the nozzle to dispense the partial atomised resins to converge at a point
- The airbrush nozzle was adjusted to allow the increase or decrease of flow.

5.9.2 Observation of the In-flight Mixing System for PU Foam Using Airbrushes

From the results obtained, it was observed that even though the reduction in time delay at each point increased the radius, height, and in effect the volume, the reduction in time with respect to heights and radii were not proportional. Therefore, it is required that the system must be fully automated to enable uniform movement to ensure that the same thickness of foam is obtained for each Z-movement of the build platform when it is incorporated with the additive manufacturing system.

5.10 Problems encountered with the in-flight mixing deposition system

- Even though the dispensed resins hit the surface mixed, homogeneity of mixture was not achieved as compared to the hand mixed process. This is due to fast cooling of the substrate because of the ambient room temperature. This could be resolved by keeping the substrate plate at an elevated temperature to enhance the mixing. This is evidenced by the application of the electric air heater to follow the substrate.
- As the resins come out in the form of spray, it is difficult to control substrate width. This is evidenced in the tracks printed with different widths even though all parameters were kept the same.
- Non-uniform thickness of tracks printed due to manual control of nozzles.

Even though the in-flight mixing using the airbrushes was able to dispense the PU reactants (polyol and diisocyanate) to mix on a surface of deposition, a continuous second layer on to a previous one by the system was not achieved, therefore, the author concluded that an alternative method to the airbrush system would be required.

CHAPTER SIX

DESIGN OF THE IN-FLIGHT MIXING PROCESS FOR POLYURETHANE FOAM USING AM TECHNOLOGY

6.1 Introduction

This chapter details the modification made on an available low cost on-site 3-D printer to in-flight mix and build PU foam. The modified X Y Z deposition machine was not able to produce a homogeneous mixture as in chapter 4. Also, the airbrush in-flight mixing system was not able to continuously lay reactants to foam on a previous layer, coupled with the system mostly hand control. Based on the information gathered on these systems and the conventional processing of PU foam, a modified in-flight mixing system was designed to be semi-automatically controlled to dispense the PU reactants to mix on the surface of deposition.

6.2 Requirements of the Designed System

Based on the information gathered in the previous analysis of this research regarding the characteristics of PU foam, the following requirements were set for the design of the in-flight mixing system to build the material. These have been divided into technical requirements and desirable characteristics.

6.2.1 Technical Requirements

These generally pertain to the technical aspects that a system must fulfil, such as performance-related issues, reliability issues, and availability issues. In this design the technical requirements are outlined as follows:

- The system must have two reservoirs that each could hold at least 50ml resin, compress, and discharge them via pipelines to the nozzles.
- The resin pipelines should be flexible enough to allow movement of nozzles

around the bed during operation and also strong and heat resistant enough to carry the resin even at high temperature (up to 100°C).

- The pipelines should incorporate valves that will control the flow of resins to the nozzles for deposition, varying the mixing ratios and secondary valves to immediately stop the flow at the end of each process.

6.2.2 Desirable Characteristics

These refer to those criteria that are not essential, therefore could be done without them or by some other means. In the design of in-flight system, they are enumerated as follows:

- A simple system which could easily be assembled and disassembled, easy to operate, and maintain.
- There should be a means of keeping the housing environment at an elevated temperature to accelerate foaming/curing.
- Nozzle holders that could easily be replaced to vary the angle of inclination between nozzles and also increase or decrease the distance between nozzle tip and surface of deposition when the need arises.

6.3 Factors Considered for the In-flight Mixing System Design

The design of the In-flight mixing system was based on the on the following under listed factors for its execution:

- The research conducted on the literature review,
- The characteristics of PU foam as detailed in chapter 3,
- Production of PU foam by conventional method (mixing uniformly the resins and casting in a mould),
- The design of PU foam deposition system, where the mixing of the two main resins mixed in a chamber before dispensing, and
- The design of the in-flight mixing system where the two main resins mixed on the surface of deposition by the influence of compressed air.

6.4 Description of the designed In-flight Mixing System

The system consists of compressed air supply which is distributed to two resin reservoirs, one containing polyol and the other diisocyanate. Two pressure controls are connected on each pipeline after the distribution junction to control the pressure acting on the resins. Each reservoir is covered with heater blanket which pre-heats and maintains the resin at the required temperature to reduce its viscosity to enable easy flow. Two pipelines, each for one of the resins are connected from the resin reservoirs to the individual nozzles. Between the resin reservoirs and the nozzles are connected two needle valves with each on one side to regulate the flow of resins from the reservoirs to the nozzles. This enables variation of mixing ratio as established in the study of PU foam characteristics documented in chapter 3 of this thesis. The nozzles are held in their housings which are extruded cylindrical portion normal to the Y-arm of nozzles holder. They are made to be screwed in and out to increase or decrease the distance between the nozzle tip and the build platform. Heated air would be distributed to the housing environment which heats the substrates to facilitate the resins reaction and speed up foaming/curing to enable another layer to be deposited on the previous one at the required rate. The platform is made to lower a height equal to thickness of a layer (equal to the height of a foamed layer) after each layer to enable another layer built on top of the previously laid one as applied to any other additive manufacturing process. The schematic diagram of the designed in-flight system is shown in Figure 6.1 and the detailed attachment is shown in Figure 6.2.

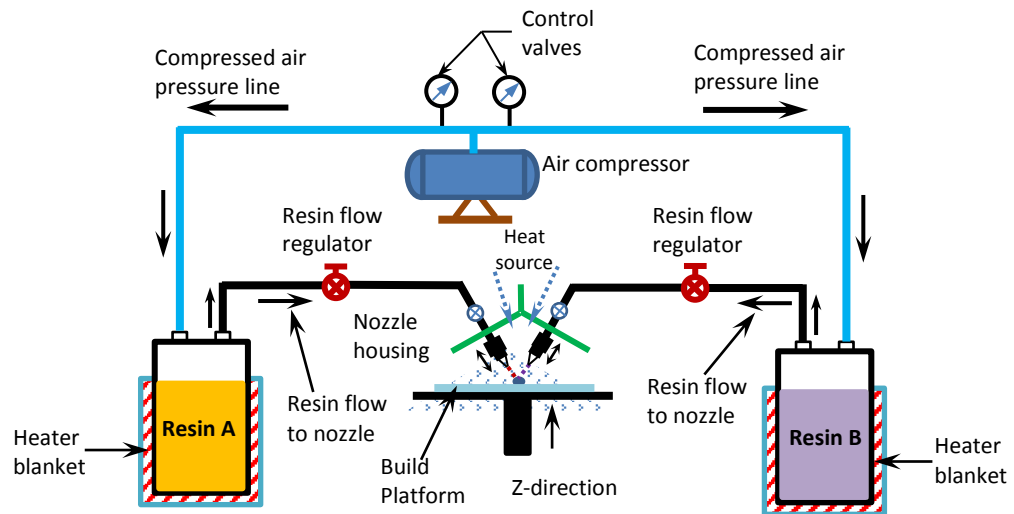


Figure 6.1: Schematic diagram of the designed in-flight mixing system

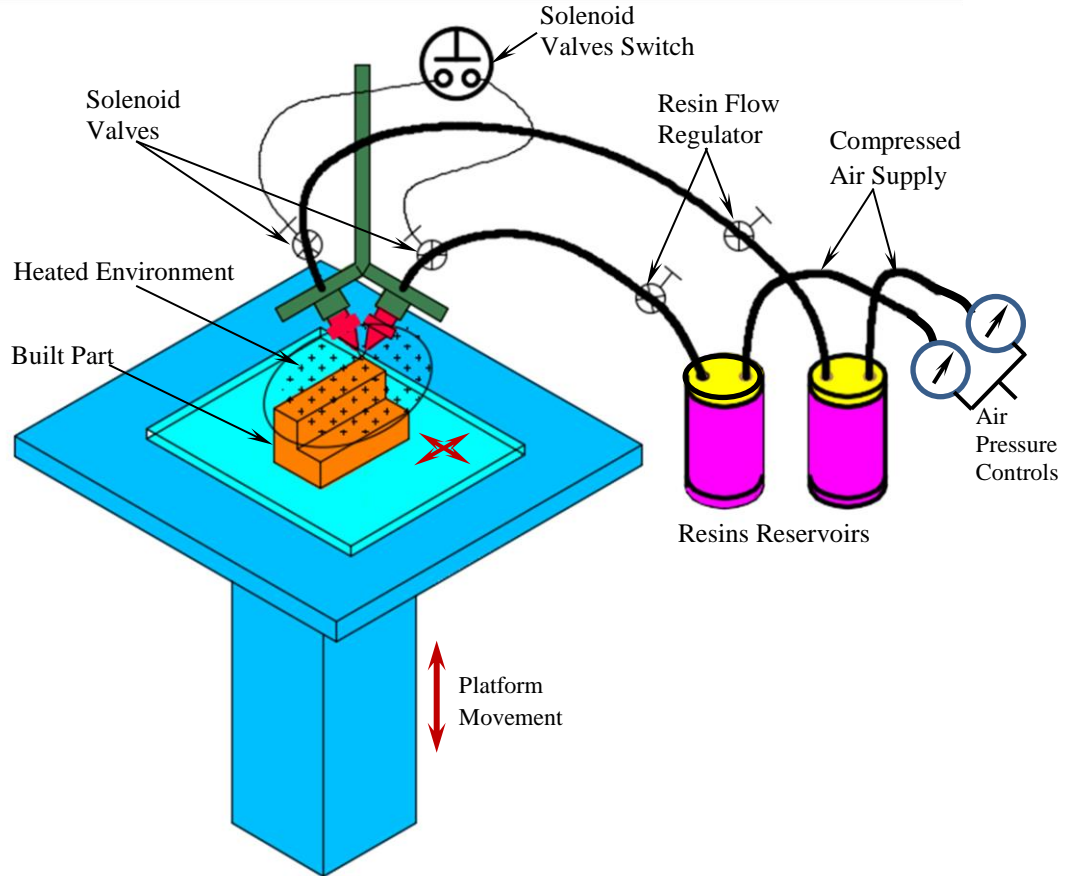


Figure 6.2: The Designed In-flight Mixing System

6.4.1 Tube Selection for the Designed System

The tubes used for all the supplies (both the compressed air to the resin reservoirs and from the reservoirs to the nozzles) are made of silicone rubber. The material offers great resistance at extreme temperatures, and is able to operate normal from -100°C to $+250^{\circ}\text{C}$ ^[205]. Throughout the system the tube has internal diameter (3 mm) and external diameter (6 mm).

6.4.2 Flow Control for Starting and Stopping Using Solenoid Valve

Accurate dispensing of resins required that once the control valves are adjusted for the mixing ratio selection and the system started, dispensing by the two nozzles start at the same time to ensure correct ratio for uniform mixing. Furthermore, once the process is completed, the flow of resins must stop immediately to avoid flow of resins through the

pipes, at the same time dripping of resins at the nozzles tip. To have minimum amount of resins remained in the pipelines and stop flow just after a process, secondary valves are installed in the lines near the nozzles to avoid dripping of resins when the valves are closed. As the pipes are to be opened and closed at the same time, two solenoid valves (an electromechanically operated valve which is controlled by an electric current through a solenoid), one on each line and the two controlled by one switch is adopted to close them at the same time. Figure 6.3 shows the circuit diagram of the solenoid valve.

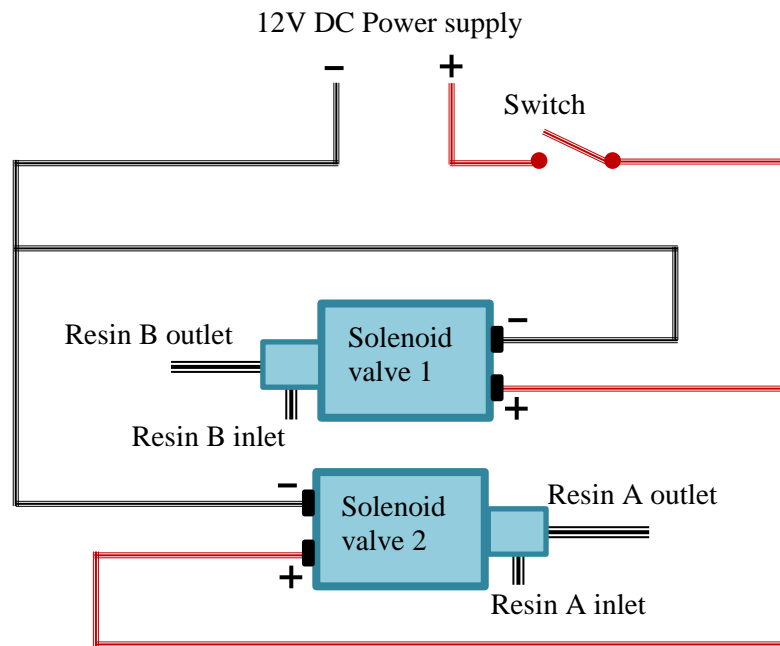


Figure 6.3: Solenoid valve circuit diagram

6.4.3 Effect of Distance Between Nozzle Tip and Build Platform

A jig was designed to hold one nozzle to spray one resin at a time to observe the flow and impact of the resins on the build surface with a gap variation. This was modelled using SolidWorks software and the parts cut from 3 mm clear Perspex using laser cutter and assembled as shown in Figure 6.4 (a). The clear colour was used for the mould to be able to observe the deposition of the resin on the build platform. The jig was designed such that the height from the surface of deposition (build platform) to the tip of the nozzle could be adjusted by changing the side plate at increments of 5 mm from 7 mm.

Three distances were considered (7 mm, 12 mm, and 17 mm) as shown in Figure 6.4 (b).

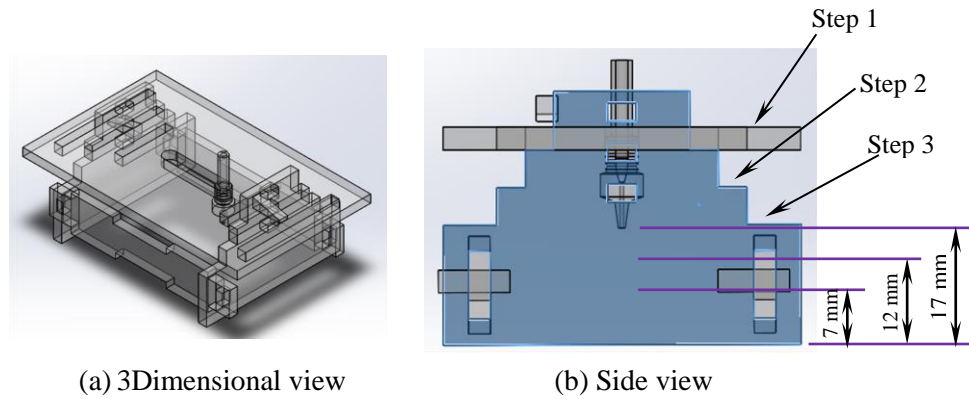


Figure 6.4: Jig for one nozzle dispensing

6.5 Replacement of PU Foam by Some Selected Non-Harmful Fluids for Trial Tests

To reduce the risk of infection by continually being in contact with the PU resins, some non-harmful fluids namely: yoghurt, honey, and syrup were chosen at random by the author to replace the resins for the remaining series of trial tests. The viscosities of these fluids were measured (Figure 6.5) to compare to the viscosities of the PU resins at varying temperatures to enable the author select the most suitable one which will also allow flow through the nozzle orifice.



Figure 6.5: Testing of viscosities of Yoghurt, Honey, and Syrup

6.5.1 Dispensing of the Selected Non-Harmful Fluids

The viscosities of the fluids were measured using the method previously employed in this research. The two dispensing units were connected to the compressor and the pressure set at 1.5 bar. The reservoir of the unit whose nozzle was held in the jig was filled with yoghurt which had been stirred to mix homogeneously. The valves of the two units were opened, even though the unit with the empty reservoir was not going to dispense any fluid. The first step of the jig from the bottom which enabled 7 mm distance between the nozzle tip and the build platform surface was used and with the compressor on, the jig was moved steadily on the build surface to print a straight track for a period of 12 seconds based on the flow. The jig was collapsed and re-assembled with the side supports that enabled 12 mm distance between the nozzle tip and the surface of deposition. The process was repeated for the 17 mm gap side support and the tracks printed were measured at three points each at random and put together for comparison.

The process was repeated for the honey and the syrup with a control amount of water (5 ml of water to 50ml of fluid in steps) to vary their viscosities. The 7 mm gap between the nozzle and the build platform was the only one used for the honey and syrup tests as this dispensed more uniform tracks when used for the yoghurt.

6.6 Discussion of the Non-Harmful Fluids Flow Test Results

The viscosity of the yoghurt in its raw state was measured three times for repeatability and the average was 214 cP, but mixing with 5ml of water to 50ml of yoghurt reduced the viscosity to 114 cP. Therefore, the test using the yoghurt was not continued.

The tracks printed by the nozzle at three different heights from the build platform are shown in Figure 6.6. The width measurement taken at three points at random along the length of the tracks are illustrated in Table 6.1.



Figure 6.6: Printed tracks of yoghurt

Table 6.1: Measurement of yoghurt tracks at different nozzle height

Nozzle tip height from surface of deposition (mm)	Average width (mm)	Average depth (mm)
7	5.8	3.2
12	6.1	2.9
17	6.3	2.8

From the results, it was observed that the track printed with the 7 mm gap was more uniform than the 12 mm and 17 mm gaps between the nozzle tip and the build platform. The author therefore suggests that the distance between the nozzle tip and the surface of deposition should be as minimum as possible to ensure that the required track width is obtained.

Figure 6.7 shows the tracks printed using the syrup and the measurements observed for the viscosities of the honey and the syrup in three states in addition to the yoghurt which passed only the first test are illustrated in Table 6.2.

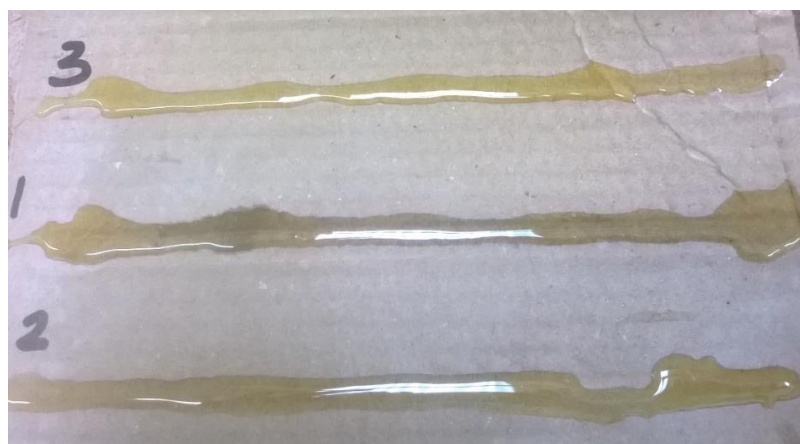


Figure 6.7: Printed tracks of honey

Table 6.2: Viscosity of fluids at different stages

Fluid	Average Viscosity (Cp)			Average Width (mm)			Average Height (mm)		
	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3
Yoghurt	214	-	-	5.8	-	-	3.2	-	-
Honey	721	479	260	2.7	3.0	3.2	1.8	1.8	1.7
Syrup	710	617	280	2.8	2.9	3.1	1.8	1.7	1.6

From the results (Table 6.2), the viscosities of the three states dispensed for the two fluids fell within the viscosity range of the PU resins at varying temperature and could therefore be used to replace the resins for the trial tests. Nonetheless, the tracks printed with the syrup were more uniform than those printed using honey and was therefore chosen by the author for the subsequent trial tests.

6.7 The Final Design of the In-flight Mixing System

The final modification of the system was the inclusion of all the sub-systems designed and manufactured or bought and incorporated to the Replicator 3-D Printer.

6.7.1 The Physical Components of the Designed In-flight Mixing Process

Figure 6.8 and Figure 6.9 show the side and front views respectively of the complete assembly with all the physical components of the attachment used to modify an available low cost 3-D Printer. The designed sub-system was used to replace the print-head of the printer, even though the electrical line from the Replicator to the print-head thermocouple was not disconnected. This was for the machine to assume that its own print-head was in place. There were other attachments such as the resins reservoirs and the tubes.

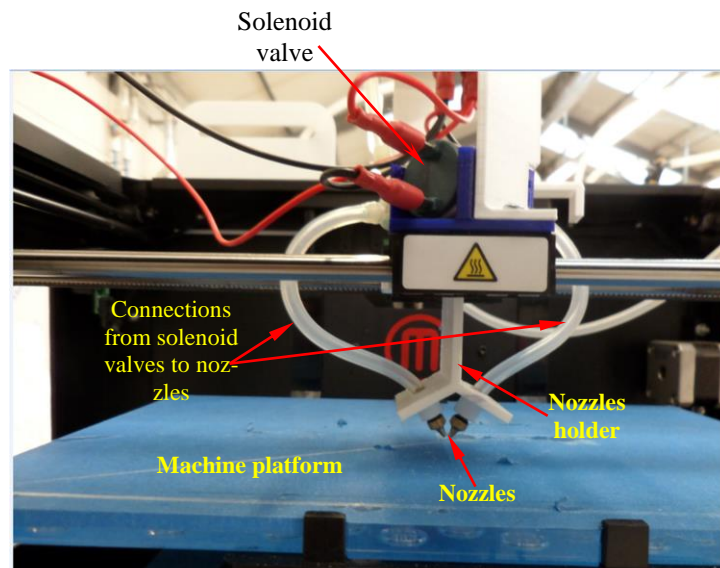


Figure 6.8: Front view of the designed attachment

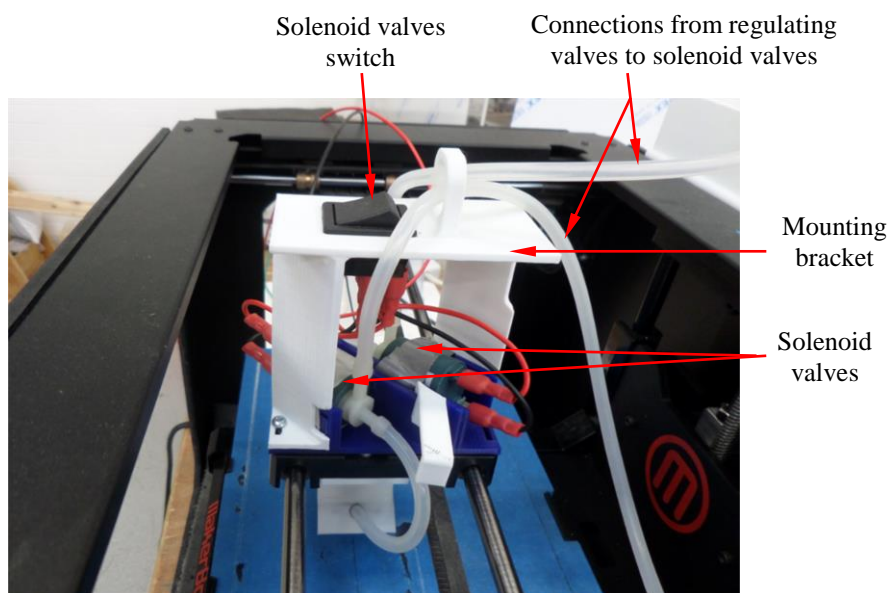


Figure 6.9: Side view of the designed attachment

6.7.2 Distance between Nozzle Tip and Build Platform Adjustment – Geometry of the Nozzle and Holder.

After series of trials, it was realised that, above 60° , the dimensions of the available nozzles did not permit distance between them and the build platform, and below 40° , the distance between them and the convergent point on the platform was too much. Therefore, three angles between the two nozzles were selected for the final tests, including 60° , 50° , and 40° . The geometries of the selected angles are illustrated in Figure 6.10. The distance between the tip of the nozzle and the build platform could be adjusted by screwing in or out the nozzles into the holder. The distance variation in x, y, and h directions for the various selected angles are modelled in Table 6.3.

The detailed drawings are documented in the appendices of this thesis.

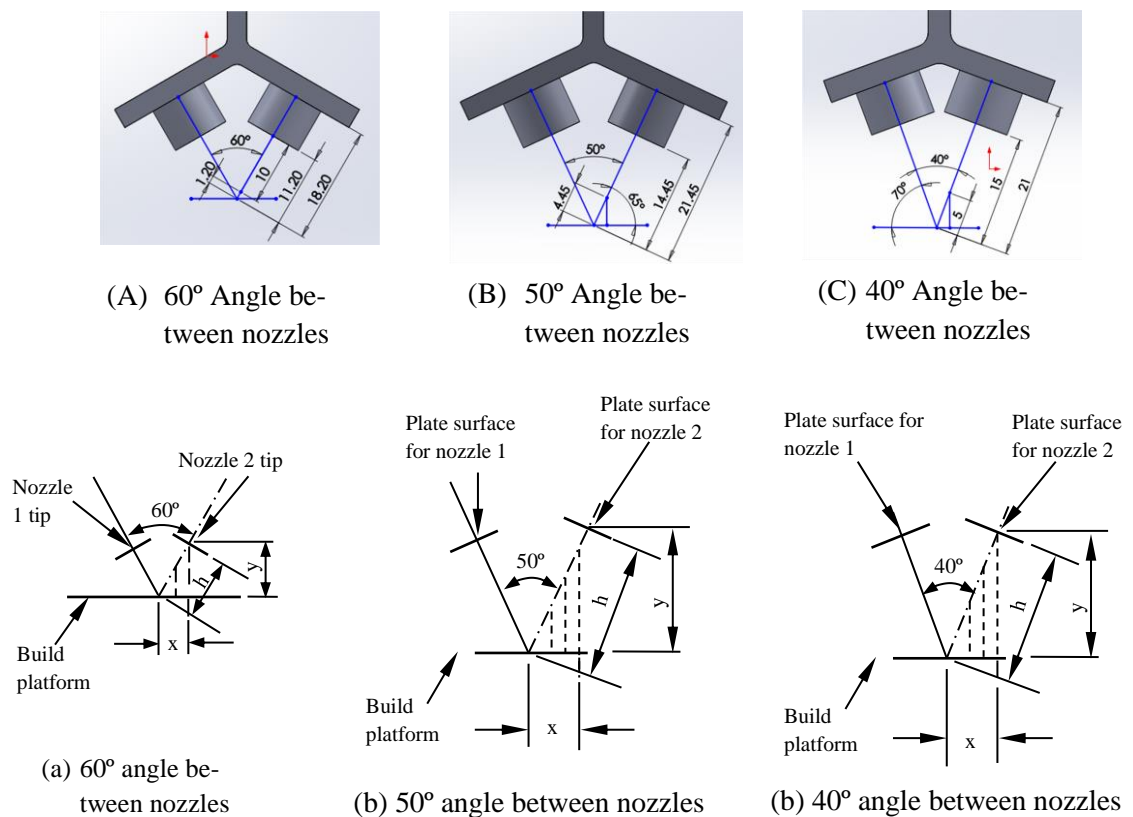


Figure 6.10: Geometry of the nozzle and holder adjustment

Note: Not drawn to scale

Table 6.3: Geometry of distance variation between nozzle tip and build platform

60 Degrees			50 Degrees			40 Degrees		
h (mm)	x (mm)	y (mm)	h (mm)	x (mm)	y (mm)	h (mm)	x (mm)	y (mm)
–	–	–	4.45	1.88	4.03	5.00	1.71	4.68
–	–	–	3.95	1.67	3.58	4.50	1.54	4.22
–	–	–	3.45	1.46	3.13	4.00	1.37	3.75
–	–	–	2.95	1.25	2.67	3.50	1.20	3.28
–	–	–	2.45	1.04	2.22	3.00	1.03	2.81
1.20	0.60	1.04	1.95	0.82	1.77	2.50	0.86	2.34
1.00	0.50	0.87	1.45	0.61	1.31	2.00	0.68	1.87
0.80	0.40	0.69	0.95	0.40	0.86	1.50	0.51	1.41
0.60	0.30	0.52	0.45	0.19	0.41	1.00	0.34	0.94

From the geometrical diagrams (Figure 6.10) and the Table 6.4, the maximum inclined distance of 60° when the nozzles were screwed in their holders was 1.20 mm. As the inclined distance from the nozzle tip to the build platform was so short, it was difficult to reduce the distance. The minimum inclined distance that could be obtained was 0.60 mm. The maximum inclined distance obtained for the 50° one was 4.45 mm whilst the minimum being 0.45 mm and the maximum for the 40° was 5.00 mm with its minimum being 0.94 mm.

6.8 Testing of the Designed In-flight Mixing Process

The final designed system was tested using the Syrup (which was found in the earlier tests to be the best non-harmful substitute among the three fluids considered to replace the PU base materials (polyol and diisocyanate).

A simple rectangular hollow block with internal dimension (80 mm x 60 mm) and external dimension (84 mm x 64 mm) shown in Figure 6.11 and ring of internal diameter (60 mm) and diameter (64 mm) as shown in Figure 6.12 were modelled using Solid-Works with extrusion of 3mm and saved in sldrt file (a), converted to slicing file (b), and subsequently to stl file (c). The model was transferred to the modified MakerBot Replicator 3–D printer for printing.

The solenoid valves connections to the 12V DC battery were checked in accordance with the solenoid valves' operating specification by the manufacturer. The two resin reservoirs were connected to the TC2000 compressor with the modification used in the previous tests and the pressure set at 1.5 bar. In all cases the solenoid valves were opened after all preliminary movements of the dispensing unit (print head) and the machine just starting to print the real object.

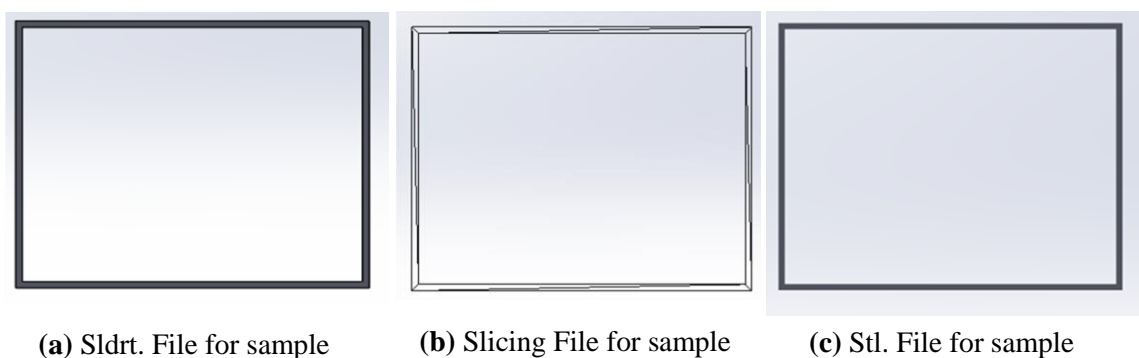


Figure 6.11: Modelled sample for testing of the designed/modified replicator

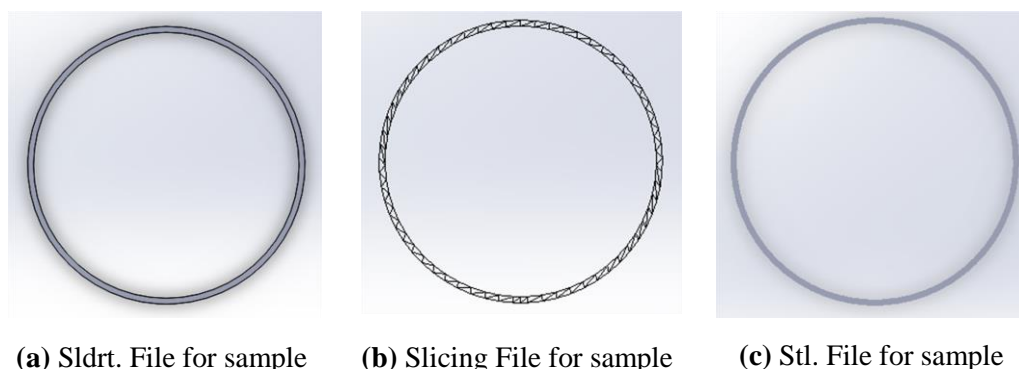


Figure 6.12: Modelled sample for testing of the designed/modified replicator

6.8.1 Testing of the Designed In-flight Mixing Process Using Syrup

The resin reservoirs were filled with the Syrup which has been mixed with water (50ml of syrup to 5ml of water) to reduce the viscosity to ensure that it is within the acceptable range for the test. One of the syrup in the containers was dyed with deep green food colouring liquid, and the other yellow which did not have effect on the viscosity when re-tested. The viscosity measured was 550 cP approximately.

The three selected angles (60°, 50°, 40°) between the nozzles were used for the dispensing using the available nozzle of orifice diameter 0.6 mm each of the two nozzles for the printer to print both the rectangles and the circles. Each test was carried out three times for repeatability. The widths and depths of the printed rectangles and circles were analysed by comparing measurements at three points on each side of the rectangles and six different points on each of the circles.

6.8.2 Testing the Designed In-flight Mixing Process Using PU Resins for 3-Dimensional Foam Product

This was the repetition of the tests using the Syrup. In this case, the syrup was replaced by the original material for this research (PU foam resins A and B). Once again, the nozzle with orifice diameter 0.6 mm with holder angle 60° was used. The 60° holder was used as it produced the best results in the immediate previous test using the Syrup. In the absence of the heater blanket the PU resins in their various reservoirs were held in hot water which had been heated to approximately 60° to elevate the resins' temperature to enable them flow through the nozzle orifice. The compressor was started and ensured that the pressure was set at 1.5 bar and the system run to dispense the resins to mix on the surface of the build platform using the same file used for printing the syrup. Once again, the widths and depths of the printed rectangles and circles were measured and compared, with three points on each side of the rectangles and six different points on each of the circles.

6.8.3 Printing of 3-Dimensional Foam Blocks Using the Designed In-flight Mixing System

To print 3-Dimensional block per the aim this research, a program was drawn using the ReplicatorG language to be able to use the available MakerBot Replicator 3-D Printer. This enabled a dwell period or pause of the machine for the period estimated for the laid foam to cure.

The default written program of ReplicatorG was modified to suit the designed Three Dimensional parts to be built. Figure 6.13 (a) and (b) are Two-Dimensional tracks of

rectangular block of length 160 mm and breadth 90mm and a triangular block of the adjacent sides 160 mm and 90 mm respectively.

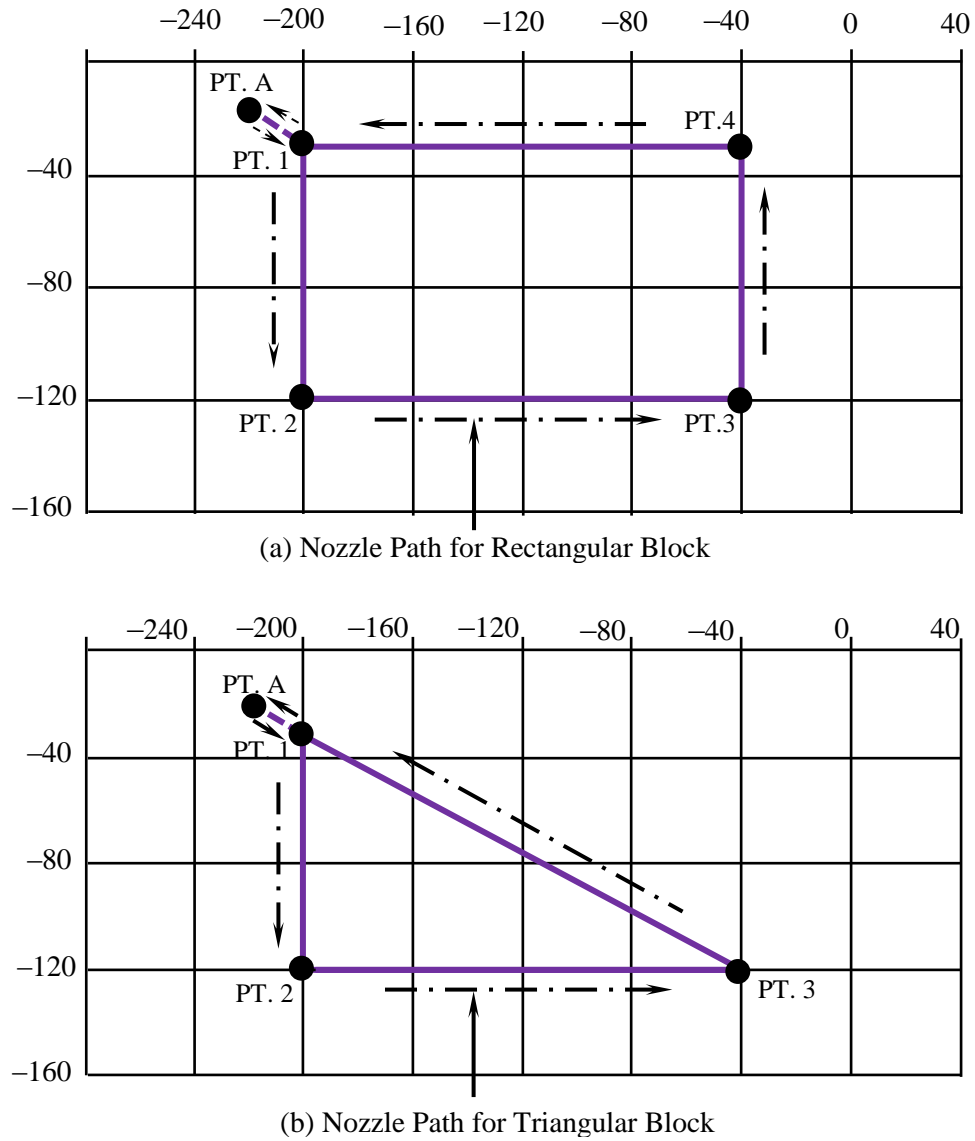


Figure 6.13: Nozzle path geometry for rectangular and triangular parts

6.8.4 Programming for Printing PU Foam Blocks

The program written for the rectangular block was to repeat the same layer two times at height difference of 3 mm and a machine linear speed of 10 mm s^{-1} . Enough dwell period 180 seconds coded as G4 was assigned to enable the dispensed foam cure before the next layer is laid. The initial distance between the nozzle tip and build platform was 2 mm. An auxiliary point “A” was included as the first point where the tool first rapidly

moves to, and continue to point 1 (PT. 1) and dwells for a machine period of P600 to allow the solenoid valves to be opened by a switch when the nozzles are just about to move from PT. 1. The solenoid valves are immediately closed when the nozzles reach PT. 1 before they go to rest for dwell at PT. A and the cycle is repeated.

The process was repeated for the triangular block for two layers, but the linear speed for the second layer was set at 8 mm s^{-1} to compare the difference. The detailed programming for the two blocks is documented in the appendices of this thesis.

To compare the scaffold structure of cross sections of the printed block at different points along the lengths and breadths, the pores of the layers on top of each other were viewed using the Alicona scanner and the SEM at different sections. As the foam is an insulator, the edge of the sample for the SEM scanner was coated with silver to make it conductive.

6.9 Test Results/Discussion of the Designed In-flight Mixing System

6.9.1 Two-Dimensional Print of Syrup

Figure 6.14 – Figure 6.16 (a) – (c) illustrate three samples each of the two figures (rectangular and circular) printed using the 60° , 50° , 40° holders.

The rectangular and circular tracks printed using the 60° nozzle holder are shown in Figure 6.14 and the dimensions are illustrated in Table 6.4.

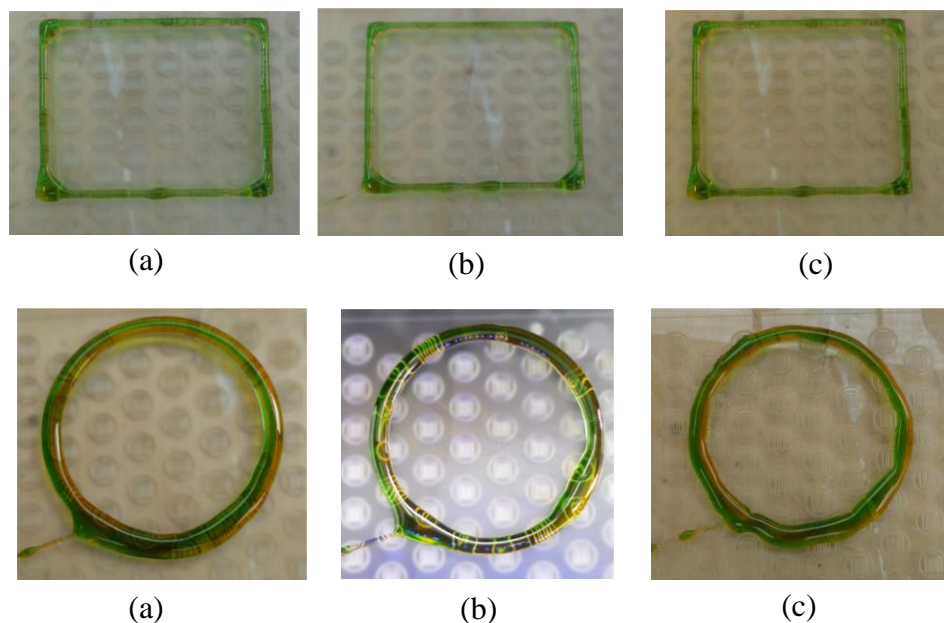


Figure 6.14: Printed samples using 60° nozzles holder

Table 6.4: Measurements of syrup tracks printed using 60° nozzle holder

Track	Layer Thickness (mm)		Layer Heights (mm)	
	Maximum	Minimum	Maximum	Minimum
Rectangular	3.1	3.9	1.5	1.9
Circular	3.6	4.3	2.7	3.4

The rectangular and circular tracks printed using the 50° nozzle holder are shown in Figure 6.15 and the dimensions are illustrated in Table 6.5.

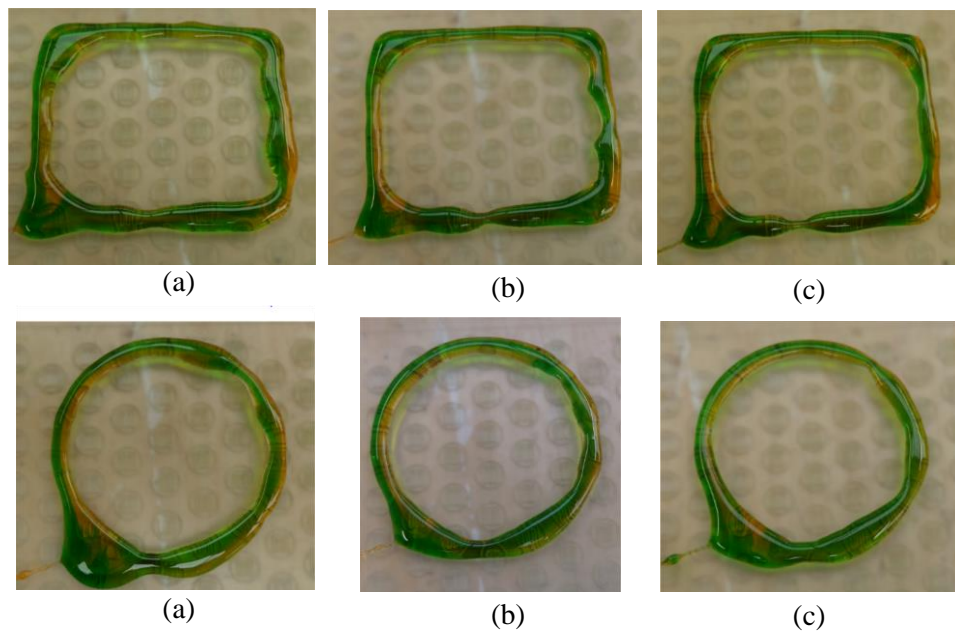


Figure 6.15: Printed samples using 50° nozzles holder

Table 6.5: Measurements of syrup tracks printed using 50° nozzle holder

Track	Layer Thickness (mm)		Layer Heights (mm)	
	Maximum	Minimum	Maximum	Minimum
Rectangular	3.1	4.3	2.5	2.7
Circular	3.8	4.5	2.8	3.5

The rectangular and circular tracks printed using the 40° nozzle holder are shown in Figure 6.16 and the dimensions are illustrated in Table 6.6.

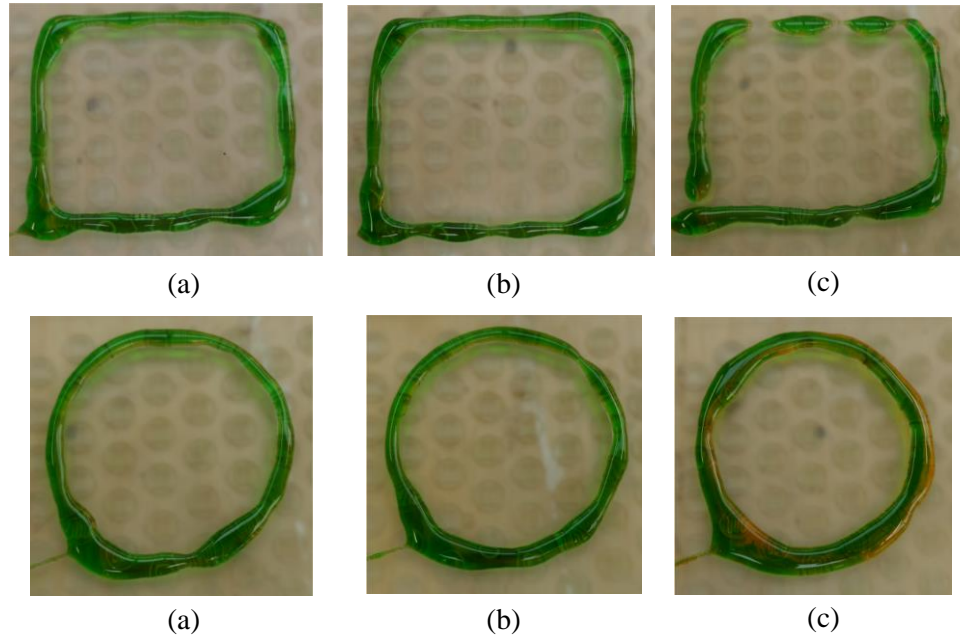


Figure 6.16: Printed samples using 40° nozzles holder

Table 6.6: Measurements of tracks printed using 40° nozzle holder

Track	Layer Thickness (mm)		Layer Heights (mm)	
	Maximum	Minimum	Maximum	Minimum
Rectangular	3.4	4.1	1.6	2.1
Circular	3.7	4.4	2.8	3.5

In all the tracks printed, even though the designed thickness was 2 mm, the layer thicknesses and heights depended on the nozzle diameter and the fluid flow. The starting point for both the circular and circular tracks had more build material as the dispensing unit stops therefore the valves are closed to stop the flow of flow completely.

This is a confirmation of the results obtained in section 5.7 (effects of dispensing delays).

6.9.2 Two-Dimensional Print of Foam Blocks

The results obtained for the printed rectangular tracks are shown in Figure 6.17. From the cured rectangular foam tracks printed, it was observed that even though the dispensed resins mixed and foamed, the layer thicknesses and the heights of the fully cured rectangular patterns were not uniform. The dimensions of the printed tracks are illustrated in Table 6.7.

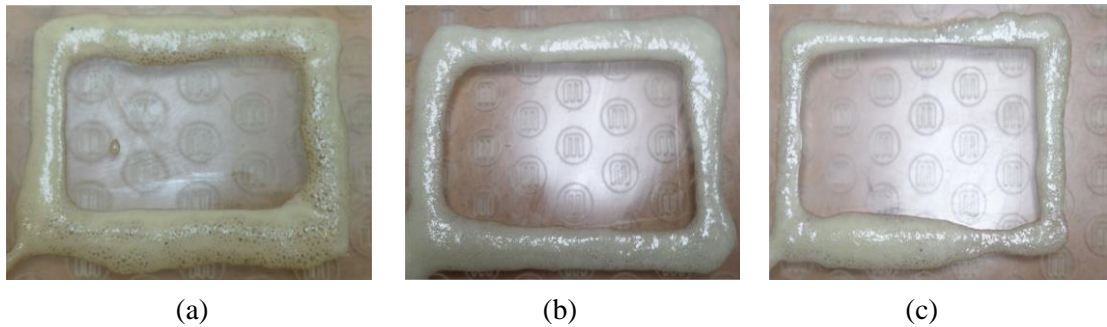


Figure 6.17: PU foam rectangular images printed using the modified in-flight mixing process

Table 6.7: Dimensions of rectangular foam tracks

Track	Layer Thickness (mm)		Layer Height (mm)	
	Minimum	Maximum	Minimum	Maximum
a	4.9	7.2	3.9	4.8
b	3.9	5.8	2.3	4.2
c	3.2	6.3	2.8	4.7

The results obtained from the printing of the circular tracks are shown in Figure 6.18 and the dimensions of the printed tracks are illustrated in Table 6.8.

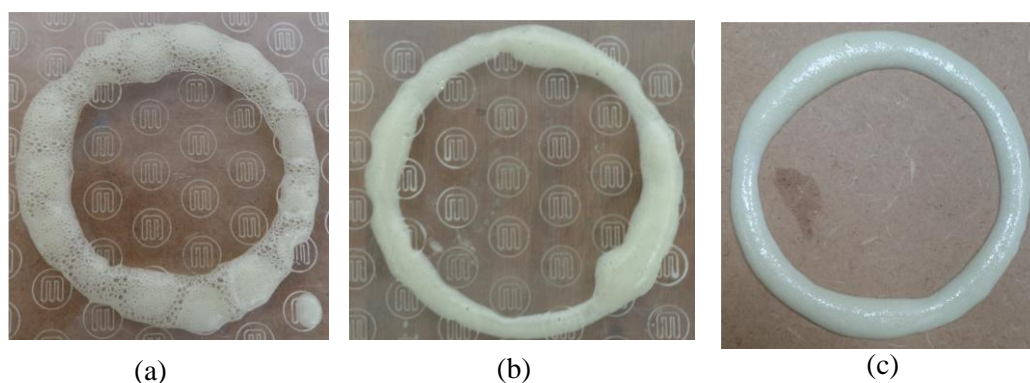


Figure 6.18: PU foam circular images printed using the modified in-flight mixing process

Table 6.8: Dimension of circular foam tracks

Track	Layer Thickness (mm)		Layer Height (mm)	
	Minimum	Maximum	Minimum	Maximum
a	5.8	7.3	4.1	4.3
b	3.3	7.2	2.1	4.0
c	3.8	5.5	2.8	4.1

6.9.2.1 Skin Effect of Single Layer Foam Track

Formation of PU foam could be a complex process as it involves two reactions running simultaneously, involving urethane forming and blowing of CO₂. The blowing of CO₂ secondarily forms urea which is not very soluble in the reaction mixture thereby tending to form separate “hard segment” phases mostly consisting of polyurea^[206, 207]. This has also been explained in section 2.3.6.

The cell opening phase of PU formation is one of the most important events since it determines air flow (i.e. fraction of open cell windows of a foam). The air flow of PU foam affects many of its physical properties^[206, 207], such as density and in effect porosity. Air flow remains a difficult property to control in industry because the mechanism of cell window rupture has not been very much research into^[30, 206, 207].

During the foaming process, there is an internal reaction that takes place with high exothermic. As the temperature of the foam rises there is heat lost from the open top surface to the ambient air^[30, 206, 207]. As a result of this, the temperature of the open top skin becomes lower than the inner core. The lower temperature profile yields slower reaction kinetics thereby, having less carbon dioxide generated in the open top skin than at the inner core of the bun^[206, 207]. This makes the top skin dense with low gas layer and becomes less dense as it gets into the inner part of the bun therefore, increasing the size of the pores from the outer surface to the inner core.

The microstructure of the cross-section of the fully cured two dimensional PU foam track printed using the designed in-flight mixing system was viewed using the Alicona scanner to check the skin effect and the image is shown in Figure 6.19. From the image, it was observed that the pores of the surface were very close and increases as it gets to the inner portion of the block. This confirms the skin effect that the inner pores of PU have larger pores due to the retained temperature for a longer period making it trap more CO₂ whilst the outer portion have smaller pores due to its fast cooling by the environment temperature with less CO₂ trapped and for a short period.

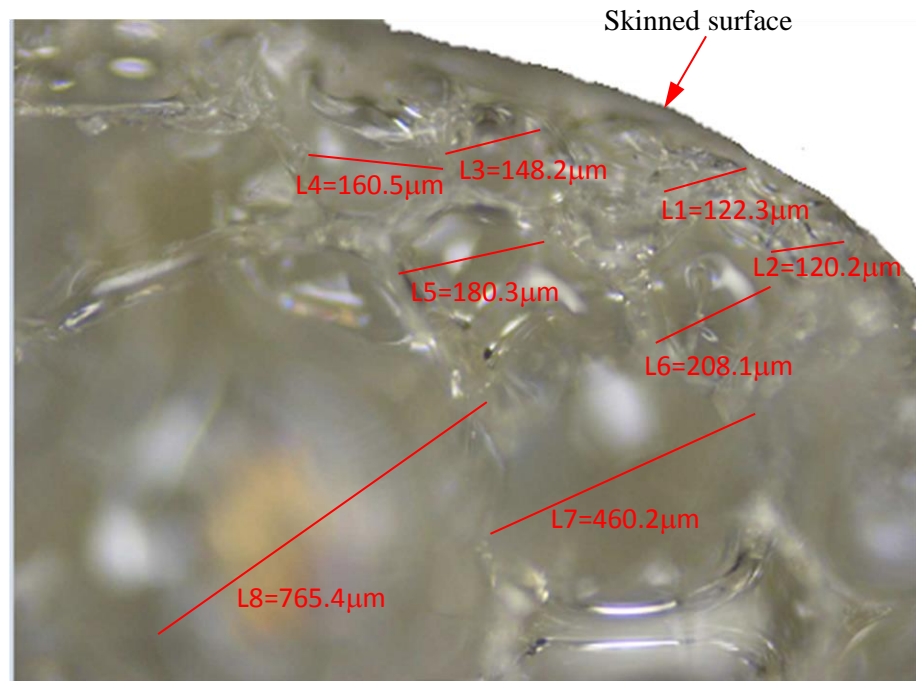


Figure 6.19: Pores variation of PU foam from the surface

6.9.3 Three-Dimensional Print of Foam Blocks

6.9.3.1 Two Layered Rectangular Built Block

The Figure 6.20 shows the image obtained for the two layered rectangular ring of 120 mm x 90 mm as the previous but at constant build speed (feed rate) of 10 ms^{-1} as indicated in the program. From the image obtained, it was observed that even though the speed was the same for the two layers, the first or base layer had a wider spread. The second layer was more uniform and thinner and as well higher than the first layer. This could be attributed to the initial higher temperature of the resins making them less viscous for the first layer. As the process continued the temperature reduced, thereby reducing the flow.

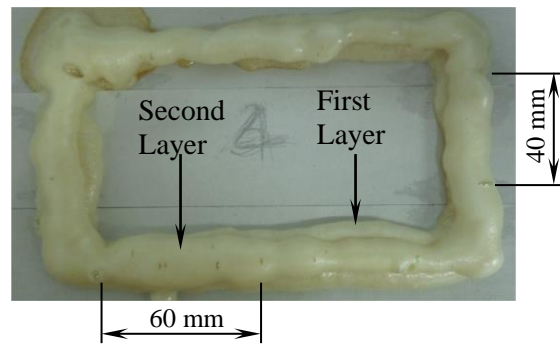


Figure 6.20: Two layered rectangular foam block

6.9.3.2 Two Layered Triangular Built Block

The results obtained for the two layered triangular block (Figure 6.21) was slightly different from the two layered rectangular block (Figure 6.20). The first layer was not as uniform as the rectangular one. This was due to the triangular block built at lower speed of 8 ms^{-1} . Once again, the second layer was more uniform than the first one as the temperature had gone down to approximately 35°C , therefore increasing the viscosity. The acute corners of triangle made the foam build more at the corners.

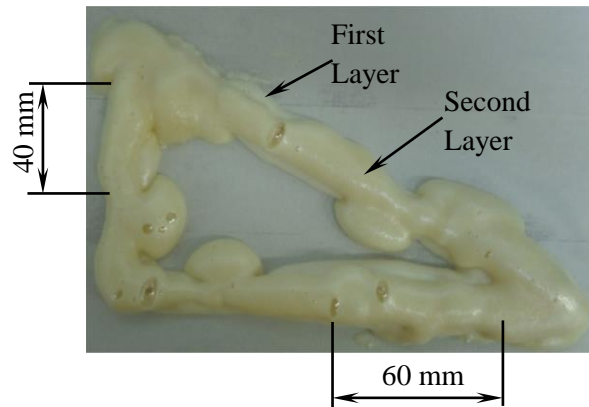


Figure 6.21: Two layered triangular foam block

6.9.4 Pores Comparison of Different Layers

The cross section of the two layered sample from the foam obtained by the modified system viewed using the Alicona scanner is shown in Figure 6.22 and the pore dimensions is as illustrated in Table 6.9. According the cross section structure along its length and breadth, the pores for the first layer looked more stretched than the pores of the second (top layer). This could be attributed to the initial temperature which was higher when the first layer was laid than when the second layer was laid. At a lower temperature the reaction is slow hence producing closer pores even though the dimensions taken were not too different from each other. The Table 6.9 shows that the average pore diameters and hence circumferences taken at random were close to each other, even though there were few far smaller ones.

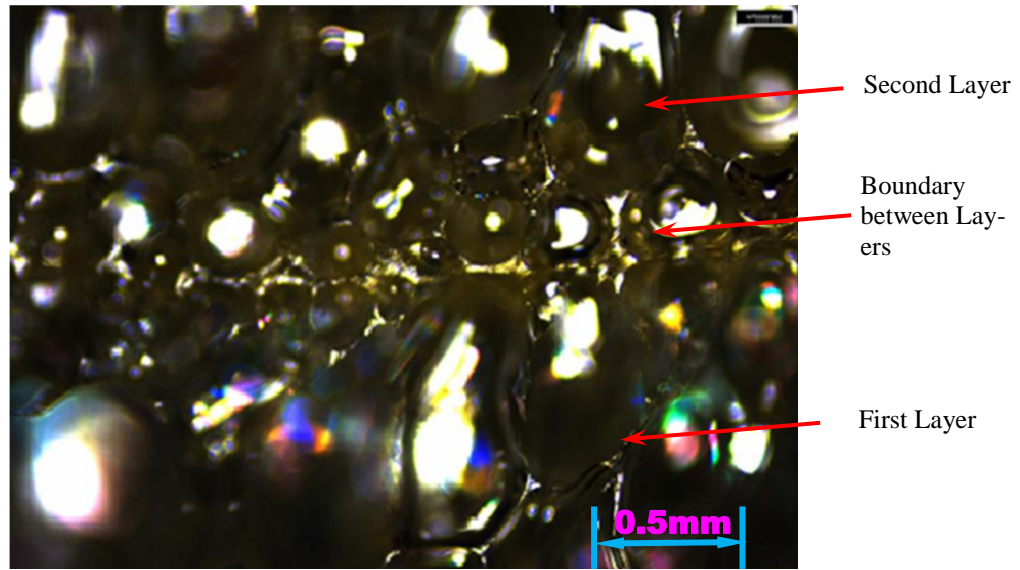


Figure 6.22: 2-Dimensional scanned image of cross section of two layered foam block

Even though there is a boundary layer between the first and second layer there was still a strong bond between the two layers, making it difficult to separate them unless by strong force or cutting. This was also confirmed in the three dimensional view shown in Figure 6.22.

Table 6.9: Table of average pore dimensions

	Length y [μm]	Length x [μm]	Angle [$^\circ$]	Average Diameter [μm]	Average Cir- cumference [μm]
L1	1113	856	84	985	3094
L2	811	449	263	630	1979
L3	949	817	269	883	2774
L4	297	195	15	246	773
L5	264	180	275	222	696
L6	963	759	26	861	2705
L7	899	813	292	856	2689
L8	1121	995	360	1058	3325
L9	413	313	91	363	1141
L10	933	815	359	874	2747
L11	646	565	355	606	1903
Average	765	614	217	689	2166

Figure 6.23 shows the three dimensional view of the cross section using the Alicona microscope which gives the clearer visualisation of the two dimensional structure shown in Figure 6.22.

To obtain approximately a uniform structure for all layers the system would require a constant heating system to maintain the same temperature of the resins throughout the process.

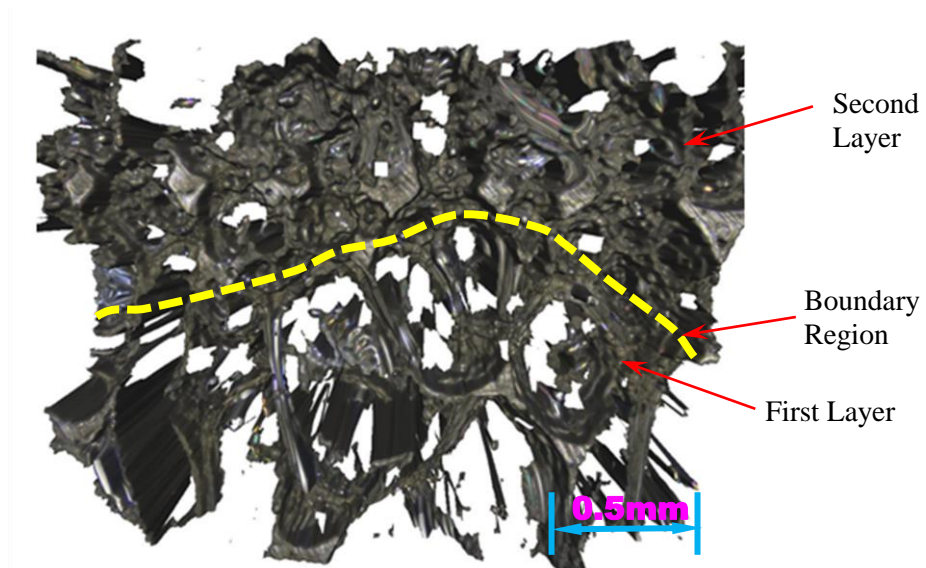


Figure 6.23: 3-D scan of two layered foam block

6.9.5 Pores Comparison of Different Layers Using SEM

The results obtained by analysing a cross section of the built block using the SEM are shown in Figure 6.24 (the combined cross section of the two layers) and Figure 6.25 (the two layers separated).

From the figures, it could be realised that the pores of the first layer were slightly stretched more than the pores of the second layer as with the first section viewed using the Alicona scanner.

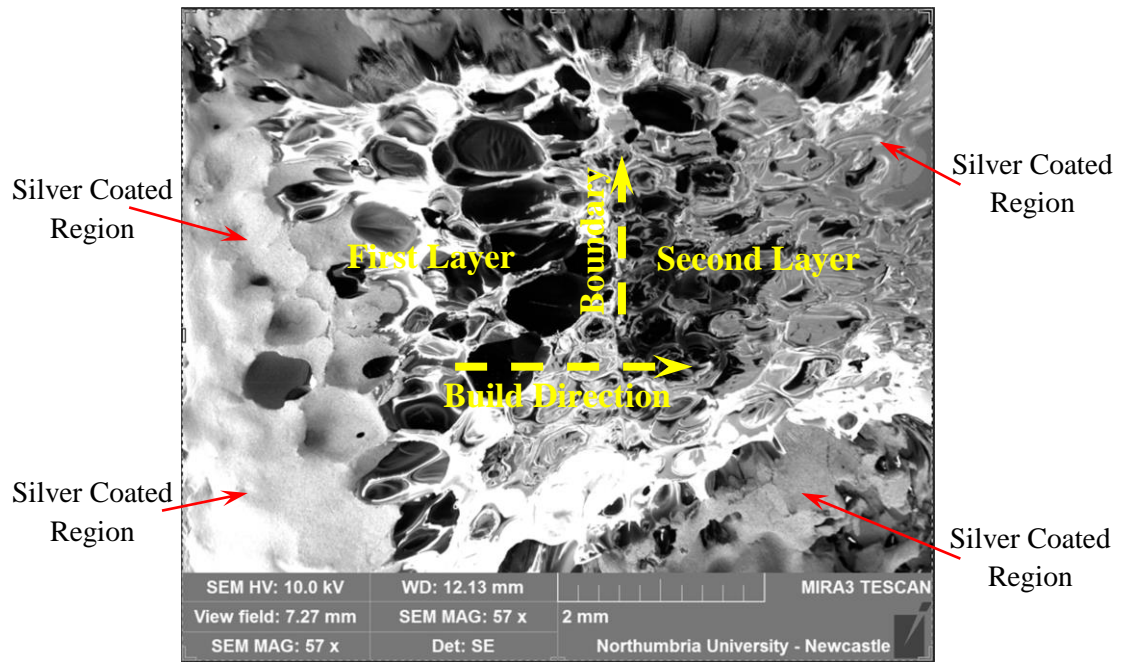


Figure 6.24: Combined structure of 3-D foam block built using the modified process - SEM view

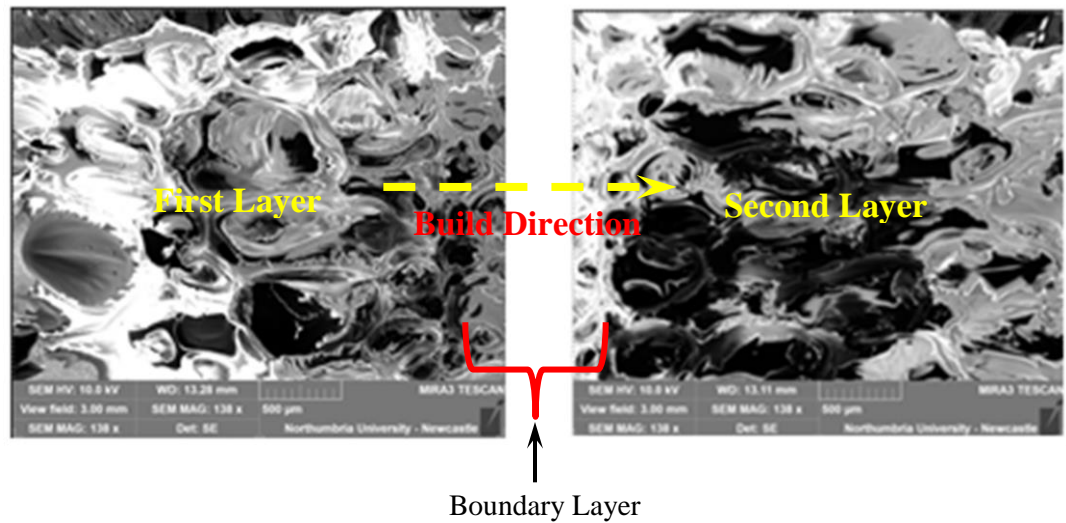


Figure 6.25: Individual structure of 2 -layered 3-D foam block using the modified process - SEM view

6.9.6 General Observations on the Parts Printed

It was observed in general that for both the rectangular and triangular blocks printed, sharp corners as in the drawings were not realised as well as non-uniform widths and

depths throughout the sections. This is similar to the general characteristics of PU foam when not confined or restricted in mould during curing as it spreads in any convenient direction. The far bigger patterns obtained compared to the dimensions on drawings is due to the original nature of PU foam as it increases in size to over 20 times depending on the mixing ratio and the nozzles used.

6.10 Maintenance of the Designed System

It is essential to always purge the system before use to remove any contamination and after use to fully drain any liquid in the system. This is done by switching off the printer and filling the reservoir with cleaning agents such as acetone and running it several times and dispensing the liquid into a container (Figure 6.26). After running through the system by acetone, it should be continued by running through it by only compressed air for at least five minutes to keep the internal part of the tubes completely dry. Also, when not in use, the set-up should be entirely covered to prevent dust from entering the interior parts of the systems.

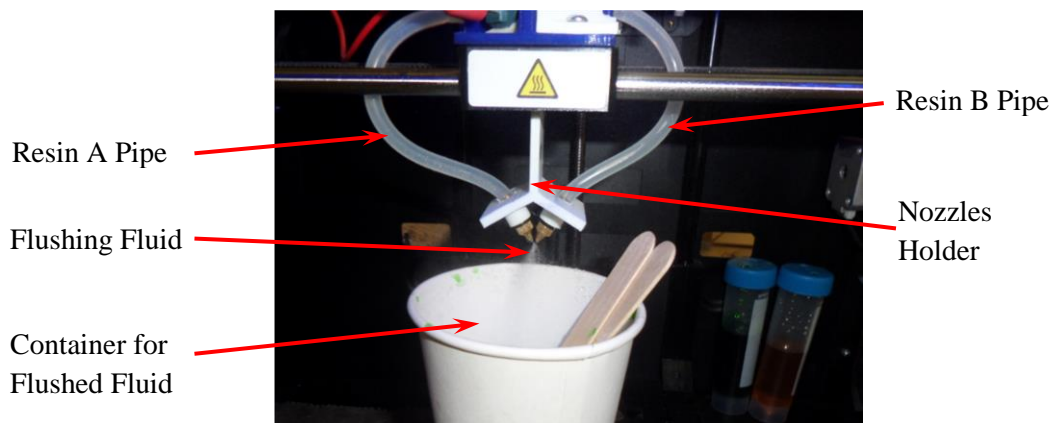


Figure 6.26: Purging of the dispensing unit of the designed In-flight mixing system

CHAPTER SEVEN

CONCLUSIONS, RECOMMENDATIONS, AND FUTURE WORK

7.0 Introduction

This chapter summarises the literature reviewed on Polyurethane foam and Additive Manufacturing technology in general. It also covers the summary of the outcome of results obtained from the investigation conducted into the characteristics of PU foam regarding its conventional production method, and adjustment on the AM technology to build the material using an in-flight mixing system. Conclusions are drawn upon the achievement of the aim and objectives set for this research. Based on the information gathered and conclusion drawn, future works are recommended to make the project fully workable.

7.1 Literature Reviewed

The literature reviewed revealed the properties of PU foam (i.e. biodegradability, biocompatibility, physical strength, and lightweight nature), making it applicable in many disciplines. Despite these versatile applications, the production method has been by mixing the constituents and casting in a mould. This research has critically reviewed the chemical compositions and the diverse applications of PU foam as documented in chapter 2. A methodology has therefore been developed which has led to the investigation of the characteristics of polyurethane foam under different conditions and have hence enabled some conclusions drawn as documented in chapter 3 of this thesis.

Also, the literature has reviewed that Additive Manufacturing is a modern technology used in many fields. The technology has not been used for the production of PU foam for any purpose due to the foaming nature of the material as it will block the orifice of the dispensing nozzle when the two main components (polyol and diisocyanate) are mixed together and foaming starts.

7.2 Polyurethane Foam Characteristics

The research has established that with the same volume of polyurethane base materials (polyol and diisocyanate) at 50:50 mixing ratio, the foaming/curing time decreases from approximately 452 seconds at room temperature (recorded at 20°C) to 54 seconds at 100°C, indicating 88% foaming/ curing time reduction. It could therefore be said that the foaming/curing time of PU reduces as the main resins (base materials) are pre-heated before mixing. Hence, where high speed system application of PU is required, pre-heating would be recommended.

The volume of cured foam varies with varying mixing ratio. With the same total volume of mixed resins, the volume increases with increasing polyol and decreasing the diisocyanate and vice versa. This is a measurement of the density in the opposite direction.

The density of PU foam is altered when the mixing ratio of the base materials (polyol and diisocyanate) is varied as well as the temperature of the base materials before mixing. From the experiments conducted, it was revealed that the density of PU foam increases with increasing part B (diisocyanate) and decreasing part A (polyol), thereby decreasing the porosity.

It has also been shown that for a particular mixing ratio (such as 50:50), the density decreases by increasing pre-heat temperature thereby increasing the porosity with the best result achieved up to 60°C.

Both the tensile and compressive strengths of cured PU foam increase by increasing the volume ratio of the PU resin Part B (diisocyanate). The tensile strength increased by 21% and the compressive strength by 49% at 40:60 mixing ratio when compared to the 50:50 mixing ratio in free foaming direction with 62% and 103% for tensile and compressive strengths respectively in the restricted foaming direction. Again, the tensile strength decreased by 8% and the compressive strength by 35% at 55:45 mixing ratio compared to the 50:50 mixing ratio in the free foaming direction with 4% and 19% for tensile and compressive strengths respectively in the restricted foaming direction.

For both the tensile and compressive strengths of PU foam, they are higher in free foaming direction (i.e. longitudinal or foaming in the direction of open side of mould) than the restricted foaming direction (i.e. lateral or foaming against the mould walls). This indicates that PU foam is anisotropic in nature based on the foaming direction,

therefore, the direction of foaming has to be taken into consideration for its effective use.

The structure of the PU foam viewed using the SEM indicates that the pore sizes are smaller for higher ratio of PU resin part B and is distorted when the resins are pre-heated before mixing, thereby affecting the porosity and density as mentioned above.

The results obtained for the viscosity test on the PU resins indicated that the viscosity of both the part A and part B dropped sharply from their initial high values of 710 cP and 535 cP to lower values of 265 cP and 235 cP respectively when heated to 30°C. From this temperature there was an easy flow through the small orifice diameter (0.6 mm) of nozzles used.

7.3 Deposition of PU Foam by Internal Mixing Using X Y Z Deposition Machine (Fisnar F4200N Brand)

An investigation was conducted on X Y Z deposition machine which dispenses liquid, originally designed for medical and laboratory type environment. The information gathered from the investigation led to the design of an attachment to the robot to satisfy the production PU foam. The modified attachment on the Fisnar X Y Z deposition system enabled the researcher use the machine to print PU foam tracks for which the principle could be adopted for the 3D printer to be able to print the material upon further modification and improvement.

7.4 In-flight Mixing of PU Foam Resins Using Airbrush

The modification of the Airbrush with the aid of air compressor had led the research to accomplish the aim of mixing of PU foam resins on the surface of deposition (build platform). By this modification, tracks of PU foam have been built by in-flight mixing of the two main constituents. The system enabled a layer of PU foam built on previous one, which proves the concept of building PU foam using AM technology. This avoids the blocking of the nozzle orifice after the mixture passing through. A second layer built on the previous one by this system and analysed by the Alicona scanner has led the re-

searcher to establish that even though there is phase separation between two layers of PU foam of one laid on already cured layer, there is a strong bond between them.

7.5 Printing of PU Foam by In-flight Mixing Using the MakerBot Replicator 3D Printer–Achievement of Aim

The modification on the MakerBot Replicator has enabled the machine print tracks of simple figures such as rectangles and circles using Syrup from two separate reservoirs with different colours, in-flight mixed and built on a platform under the influence of compressed air. These prints from stl files is a proof of concept that the PU foam could be built by in-flight mixing of the base materials (polyol and diisocyanate) on the surface of deposition using the modified Additive Manufacturing system.

The use of the ReplicatorG software enabled the researcher draw a program using the G codes, M codes, and other auxiliary codes to use the MakerBot Replicator 3-D printer to print two layers of PU foam, one atop the previous ones (creating a Three- Dimensional block). This proofs the concept of printing PU foam using Additive Manufacturing process which is the main aim of this research. The structural view of the parts printed using the Alicona scanner showed that even though there is boundary between two printed layers, there is a strong bond between the printed layers.

7.6 Uniqueness and Originality of the Research

This research was unique in the following areas:

- Establishment of the characteristics PU foam physical properties based on its production process modification
- Development of Additive Manufacturing system that can print 3-D PU foam at different mixing ratios
- Development of system that can dispense two reacting separate fluids to mix on a surface.

7.7 Dissemination of Research Findings via Conferences and Journal

The research findings have enabled the researcher written the following Conference or Journal Papers and intend writing more papers out of the findings:

- ***Title of Paper:*** Advances in Additive Manufacturing Processes
Conference: Applied Research Conference of Africa (ARCA) – 2013
- ***Title of Paper:*** Effect of Varying Mixing Ratios and Pre-Heat Temperature on the Mechanical Properties of Polyurethane (PU) Foam
Conference/Journal: The Manufacturing of Engineering Society International Conference, MESIC–2014, Published in Science Direct Journal, 2016
- ***Title of Paper:*** Effect of Varying Mixing Ratios and Foaming Direction on Polyurethane Foam for Additive Manufacturing Applications
Conference: Conference on Rapid Design, Prototyping and Manufacturing (CRDPM) – 2015
- ***Title of Paper:*** Additive Manufacturing: Past, Current, and Future Development
Journal: International Journal of Rapid Manufacturing – Under Review
- ***Title of Paper:*** Additive Manufacturing Technology Applications
- ***Conference:*** Northumbria University Research Conference – 2014
- ***Title of Paper:*** Application of Additive Manufacturing Technology for Lightweight Medical Scaffold using Polyurethane foam.
Conference: Northumbria University Research Conference – 2015

The researcher attended and presented at all the above mentioned Conferences. The full Papers of the above Conferences are covered in the appendices of this thesis.

7.8 Conclusions

The research has undertaken a critical review of Polyurethane foaming processes, medical application, and characteristics of AM technologies to establish the feasibility and application of AM technology to produce Polyurethane foam 3D structures. This re-

search has demonstrated the effect of resin mixing ratios, temperature, foaming direction on the density, porosity, tensile strength, and compressive strength of PU foam to establish a platform for selection and development of a suitable system to print the material via an Additive Manufacturing process.

Analysis of the single layer foam block showed that during PU foaming process, the high exothermic which is caused by an internal reaction decreases at the open top surface due to the heat loss from the surface to the ambient air. The surface therefore has lower temperature than the inner core making the reaction there slower and hence, less carbon dioxide generated in the open skin than the inner core of the bun. This makes the top skin dense with low gas layer, and becomes less dense as it gets into the inner part of the bun.

The material composition and hence physical properties can be controlled as and where required. The properties are dependent upon the end use application, deposited via the proposed Additive Manufacturing process developed in this research.

Three methods of deposition of PU foam structures were investigated. Although the internal mixing and the air assisted mixing did not provide controlled repeatable results, the pressure sprayed inflight mixing was demonstrated to manufacture multilayer objects.

Based on the investigations conducted, a proof of concept in-flight mixing system has been developed as an attachment to the MakerBot Replicator which has been used to manufacture PU foam. The foam produced using the developed system was tested using the Alicona scanner giving an average pore diameter of 689 μm , hence an average circumference of 2166 μm (2.17 mm). Previous research demonstrates that the pore size allows flow of fluids such as blood, diffusion of waste products out of the scaffold, cell infiltration, and vascularization, therefore making it suitable for use as medical scaffolds.

Based on the above stated achievements, it can be concluded that the aim and objectives set for this research have been achieved.

7.9 Recommendations for Future Work

- The research initiated in this project can further be developed in the following areas: Improved temperature control of reactants; by designing and building a dispensing head which would have a heating system that could be controlled to constantly heat the resins to the required temperature to speed up the foaming/curing process
- Improved pressure and flow control of reactants; by designing and building a system that would be incorporated with valves that could be digitally controlled to accurately vary the mixing ratio. These would be achieved by liaising with the industry to incorporate the design to modify the existing 3D printer to achieve the full benefits of this research
- Improved build environment temperature control and extraction of air; by building the PU foam in an enclosed housing to maintain the supply of heat and incorporate a fume/air extractor for air and fume extraction
- Modelling of in-flight mixing to optimise the expansion and curing of PU foam to make the production more economical than the traditional methods
- Design of a versatile system which will be able to meter and mix chemicals or constituents of any liquid on a surface or in a chamber in small and large sizes
- The inclusion of some of the PU additives such as: cross-linkers, chain extenders, blowing agent surfactants, plasticisers, etc. to enable the material fully usable for the intended purpose (such as medical scaffold).
- Produce multi-graded material based on mixing ratio, pre-heat temperature, and expansion direction, which would enable the material used in different part of a system
- Introduce of a system such as CNC milling to level the surface of a built layer to provide a level platform and an interlocking pore surface for the next layer. This would also reduce the effect of uneven layer expansion in the Z direction and control Z accuracy.

7.10 Limitations and Difficulties Encountered During the Research

Even though certain chemicals and aids such as blowing agents, cross-linkers, Surfactants, etc. are required in the processing of PU foam to ensure sufficient control to obtain commercial products, this research was limited to only the base materials (polyol and diisocyanate) which are the main constituents. The major equipment used such as the 3-D printer and compressor were based on the available on-site equipment.

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APPENDICES

A1 DETAILED DESIGNED DRAWINGS FOR NOZZLE HOLDER

A1.1 Detailed Drawings of Nozzle Holders at Different Angles

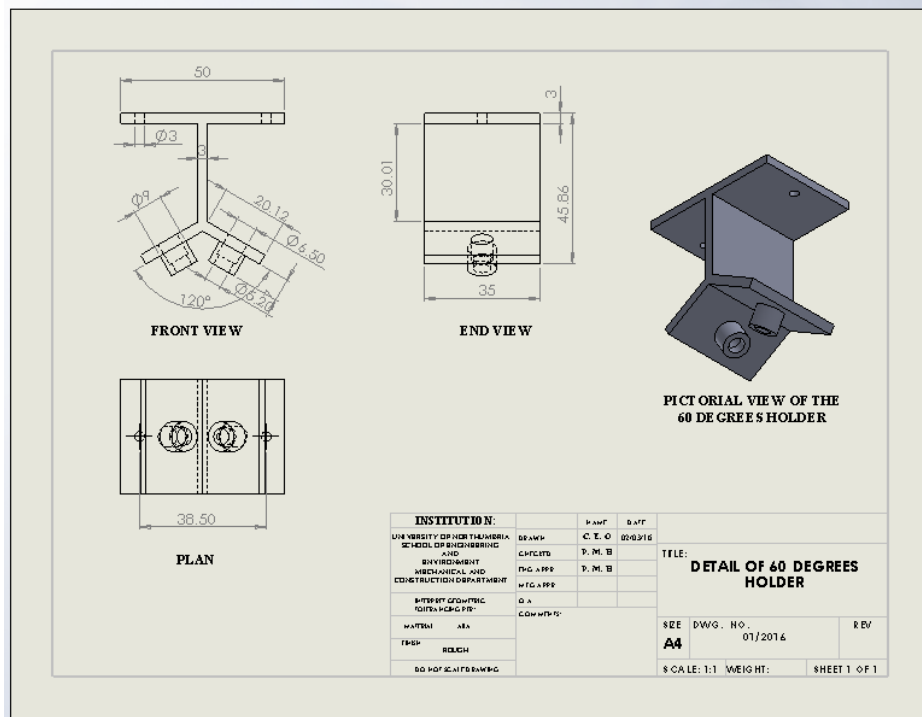


Figure A1.1: Detailed drawing of 60 degrees holder

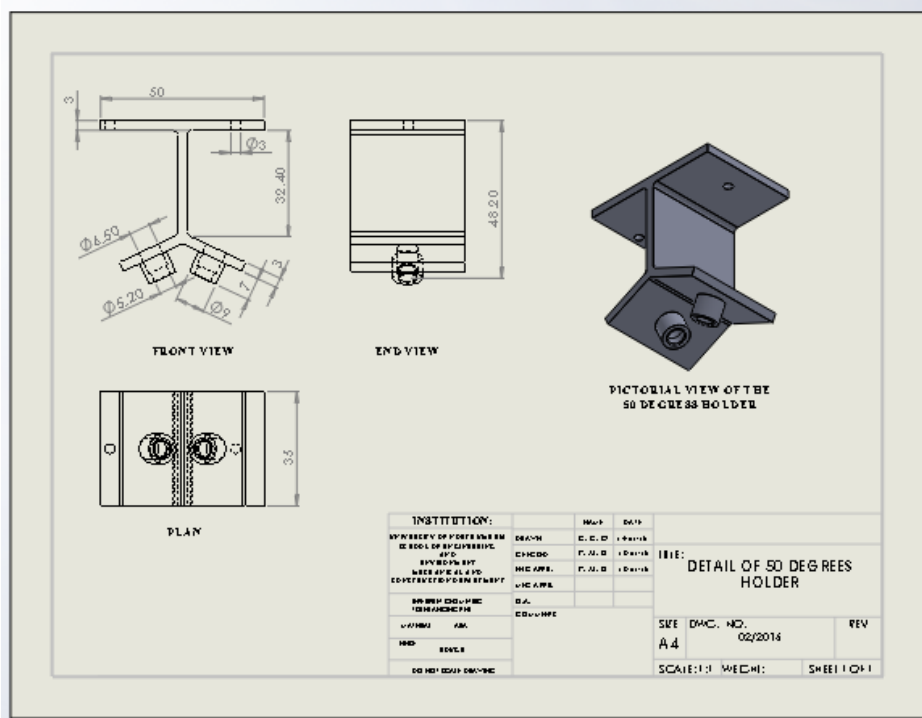


Figure A1.2: Detailed drawing of 50 degrees holder

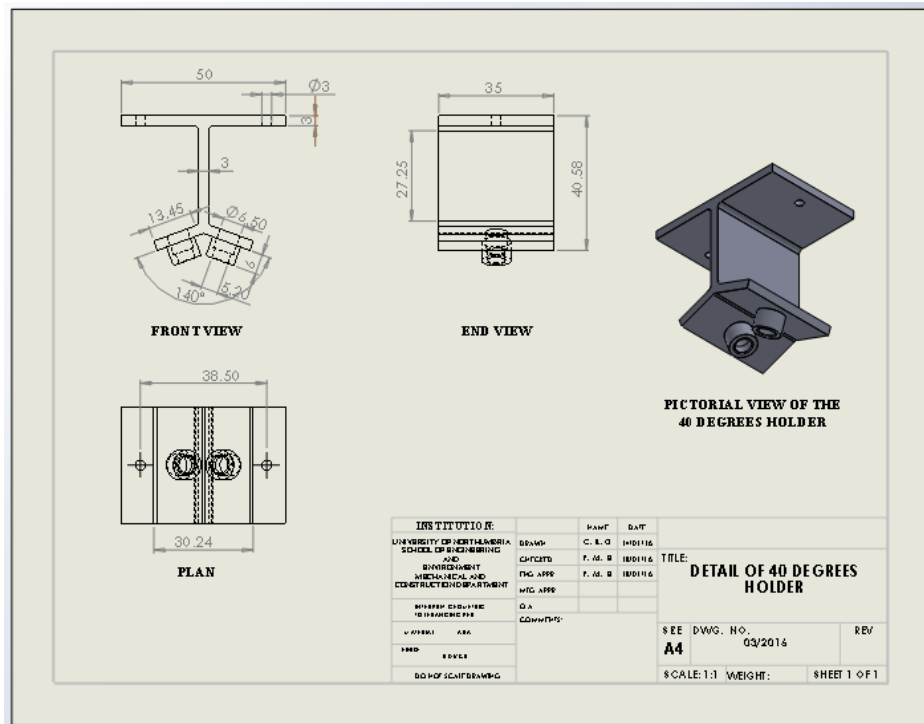


Figure A1.3: Detailed drawing of 50 degrees holder

A2: Back Cover of the Modified/Designed In-flight System



Figure A2.1: Back View of the Modified System

A3 DETAILED MODIFIED REPLICATORG PROGRAM FOR THE PRINTED PARTS

A3.1 Modified Program for 2-Layer Rectangular Block

; generated by Slic3r 0.7.1 on 2016-06-09 at 15:32:17

```
; charles set up
; layer_height = 2
; perimeters = 1
; solid_layers = 1
; fill_density = 0.4
; nozzle_diameter = 3
; filament_diameter = 5
; extrusion_multiplier = 1
; perimeter_speed = 20
; infill_speed = 15
; travel_speed = 120
; extrusion_width_ratio = 0
; scale = 1
; single wall width = 3.68mm
M104 S10; set temperature
(**** start.gcode for The Replicator, single head ****)
M103 (RPM off)
M73 P0 (enable build progress)
G21 (set units to mm)
G90 (set positioning to absolute)
(**** begin homing ****)
G162 X Y F2500 (home XY axes maximum)
G161 Z F1100 (home Z axis minimum)
G92 Z-2 (set Z to -5)
G1 Z20.0 (move Z to "0")
; G161 Z F100 (home Z axis minimum)
; M132 X Y Z A B (Recall stored home offsets for XYZAB axis)
(**** end homing ****)
; G1 X60 Y-60 Z20 F3300.0 (move to waiting position 150 z)
G130 X0 Y0 A0 B0 (Lower stepper Vrefs while heating)
G130 X127 Y127 A127 B127 (Set Stepper motor Vref to defaults)
M108 R3.0 T0

G0 X-200 Y-30 (Position Nozzle X-110.5 Y-74 )
G0 Z10    (Position Height)
M108 R4.0    (Set Extruder Speed)
M101        (Start Extruder)
```

(**** end of start.gcode ****)

G90 ; use absolute coordinates

G21 ; set units to millimeters

M106 S89

G1 Z2.000 F2500

G1 X-220 Y-15

G1 X-200 Y-30

G4 P600

G1 X-200 Y-120

G1 X-40 Y-120

G1 X-40 Y-30

G1 X-200 Y-30

G1 X-220 Y-15

G4 P60000

G92 E0

G1 Z5.000

G1 X-220 Y-15

G1 X-200 Y-30

G4 P600

G1 X-200 Y-120

G1 X-40 Y-120

G1 X-40 Y-30

G1 X-200 Y-30

G1 X-220 Y-15

G4 P600

M107

(***** End.gcode*****)

M73 P100 (End build progress)

G0 Z80 (Send Z axis to bottom of machine)

M18 (Disable steppers)

;M109 S0 T0 (Cool down the build platform)

M104 S0 T0 (Cool down the Right Extruder)

M104 S0 T0 (Cool down the Left Extruder)

G162 X Y C (Home XY endstops)

M18 (Disable stepper motors)

M70 P5 (Charles Making Things!)

M72 P4 (Play Ta-Da song)

(*****end End.gcode*****)

; filament used = 9513.3mm (186.8cm3)

A3.2 Modified Program for 2-Layer Triangular Block

; generated by Slic3r 0.7.1 on 2016-06-09 at 15:32:17

```
; charles set up
; layer_height = 2
; perimeters = 1
; solid_layers = 1
; fill_density = 0.4
; nozzle_diameter = 3
; filament_diameter = 5
; extrusion_multiplier = 1
; perimeter_speed = 20
; infill_speed = 15
; travel_speed = 120
; extrusion_width_ratio = 0
; scale = 1
; single wall width = 3.68mm
```

```
M104 S10 ; set temperature
(**** start.gcode for The Replicator, single head ****)
M103 (RPM off)
M73 P0 (enable build progress)
G21 (set units to mm)
G90 (set positioning to absolute)
(**** begin homing ****)
G162 X Y F2500 (home XY axes maximum)
G161 Z F1100 (home Z axis minimum)
G92 Z-2 (set Z to -5)
G1 Z20.0 (move Z to "0")
; G161 Z F100 (home Z axis minimum)
; M132 X Y Z A B (Recall stored home offsets for XYZAB axis)
(**** end homing ****)
; G1 X60 Y-60 Z20 F3300.0 (move to waiting position 150 z)
G130 X0 Y0 A0 B0 (Lower stepper Vrefs while heating)
G130 X127 Y127 A127 B127 (Set Stepper motor Vref to defaults)
M108 R3.0 T0

G0 X-200 Y-30 (Position Nozzle X-110.5 Y-74)
G0 Z10 (Position Height)
M108 R4.0 (Set Extruder Speed)
M101 (Start Extruder)
(**** end of start.gcode ****)
G90 ; use absolute coordinates
```

G21 ; set units to millimeters

M106 S89

G1 Z2.000 F2000

G1 X-220 Y-15

G1 X-200 Y-30

G4 P600

G1 X-200 Y-120

G1 X-40 Y-120

G1 X-200 Y-30

G1 X-220 Y-15

G4 P60000

G1 Z5.000

G1 X-220 Y-15

G1 X-200 Y-30

G4 P600

G1 X-200 Y-120

G1 X-40 Y-120

G1 X-200 Y-30

G1 X-220 Y-15

G4 P600

M107

(***** End.gcode*****)

M73 P100 (End build progress)

G0 Z80 (Send Z axis to bottom of machine)

M18 (Disable steppers)

;M109 S0 T0 (Cool down the build platform)

M104 S0 T0 (Cool down the Right Extruder)

M104 S0 T0 (Cool down the Left Extruder)

G162 X Y C (Home XY endstops)

M18 (Disable stepper motors)

M70 P5 (Charles Making Things!)

M72 P4 (Play Ta-Da song)

(*****end End.gcode*****)

; filament used = 9513.3mm (186.8cm3)

JOURNAL/CONFERENCE PAPERS DEVELOPED

C1.1 APPLIED RESEARCH CONFERENCE IN AFRICA (ARCA), – 2014

Title of Paper: Advances in Additive Manufacturing Processes

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ABSTRACT

Additive Manufacturing (AM) which is also referred as Three Dimensional Printing (3DP), Solid Freeform Fabrication (SFF) or Rapid Prototyping (RP) is a layer-by-layer technique of producing a three-dimensional (3D) objects directly from a digital model. The technique is used in engineering for prototyping, tooling, direct part manufacturing, maintenance and repair. Additive Manufacturing accounted for £1.2b (\$2b) across all industries in worldwide sales of materials, equipment, and services in 2012, and is expected to reach £2.4b (\$4b) by 2015. Additive Manufacturing is considered to be the breakthrough disruptive technology which permits end-products to be grown from materials such as inks, dielectrics and powders in a layer-wise manner. Even though the technique has had remarkable improvements since its emergence over 25 years ago, still faces several technical challenges related to material characterization and availability compared with other conventional techniques. This paper reviews the current commercially available Additive Manufacturing processes by describing generics and specifics as well as the build material characteristics. It also presents the “State of the Art” of Additive Manufacturing Technology and outlines the strengths and weaknesses of the techniques. Finally, several case studies are discussed in addition to the real life application of these techniques which will enable readers to understand and potentially exploit these emerging technologies.

Keywords: Additive Manufacturing, Three Dimensional Printing, Solid Freeform Fabrication, Direct Part Manufacturing, Rapid Prototyping.

1. Introduction

Additive Manufacturing (AM) which is the official industry standard term (ASTM 2792) for all applications of the technology encompasses many technologies including subsets such as: Additive Fabrication, Rapid Prototyping, 3-Dimensional Printing (3DP), Layer Manufacturing, and Solid Freeform Fabrication (www.additivemanufacturing.com, 2014). Unlike conventional machining techniques where material is removed incrementally until the desired shape or dimensions are achieved, AM is a layer-by-layer technique of producing three dimensional solids generated directly from 3D model data in which one layer is formed atop the previous one until the required geometry or shape is obtained. Whilst subtractive processes start from the top down, Additive processes start from the ground up (Nagel et al, 2012). Additive Manufacturing technology amounted to £1.2b (\$2b) in the sales of materials, equipment, and services in 2010 across all industries worldwide and is expected to reach £2.4b (\$4b) by 2015 (www.raeng.org.uk, 2013; Wohlers', 2011).

When Additive Manufacturing is fully understood and utilised correctly, an impressive niche and cost saving are possible. Parts and devices that are geometrically complex and have graded material compositions which otherwise are impossible to fabricate by conventional method as a whole can now be fabricated by AM technologies as a single customised component (Chu et al,

2008). The technology has tremendously helped trim weeks, even months of design, prototyping and manufacturing time whilst avoiding costly errors and improving product quality.

2. Additive Manufacturing Technology Advancements

2.1. Industry Growth

Figure 1 shows the percentage of cumulative industrial additive manufacturing systems installed in various countries from 1988 to 2012. Whereas the U.S. continues to lead by a large margin, Japan, Germany, and China follow as second, third, and fourth respectively as the largest installed bases (Vaezi, 2013).

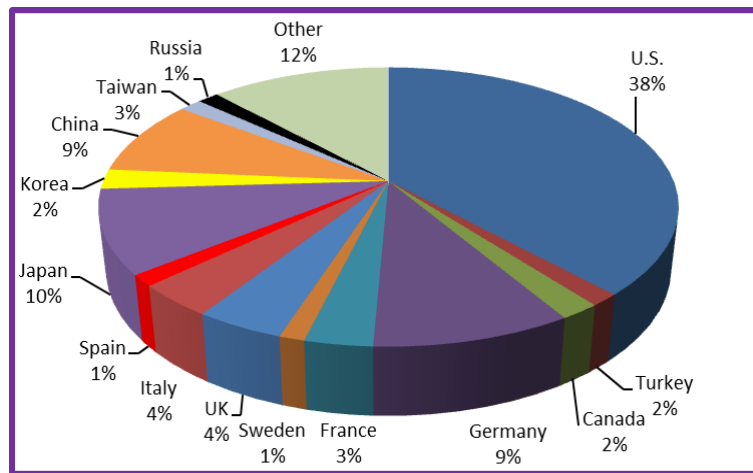


Figure 1: Countries Participation in Additive Manufacturing from 1988–2012 (Cumulative AM) (Vaezi, 2013; www.tctmagazine.com, 2013).

2.2. Additive Systems Manufacturers

The demand for products and services from Additive Manufacturing technology keeps on increasing from time to time. Therefore, system manufacturers of AM are striving to meet the demand of users in various categories. Thirty-five manufacturers from different parts of the world produced and sold AM systems in 2009 as against 34 in 2008. Figure 2 shows the 2009 unit sales market shares among manufacturers worldwide (Wohlers', 2010).

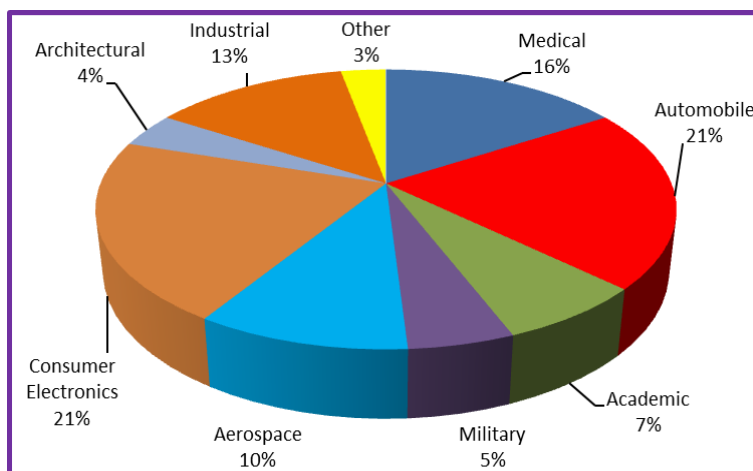


Figure 2: Additive Systems Manufacturers Worldwide (Vaezi, 2013; Wohlers', 2010).

2.3. Revenue Split of AM Equipment Customers - 2012

According to Wohlers' report (Royal Academy of Engineering, 2013), it is observed from the chart (Figure 3) that Automobile and Consumer Electronics both led with 21% each of the overall revenues by Additive Manufacturing technologies. The Medical sector contributed 16% which puts them behind only Automobile and Consumer Electronics, both being key users of the AM technology. However, the main difference between them is that Medical industry uses the AM technology for direct production of products, whereas, the others use it primarily for prototyping purposes (Royal Academy of Engineering, 2013).

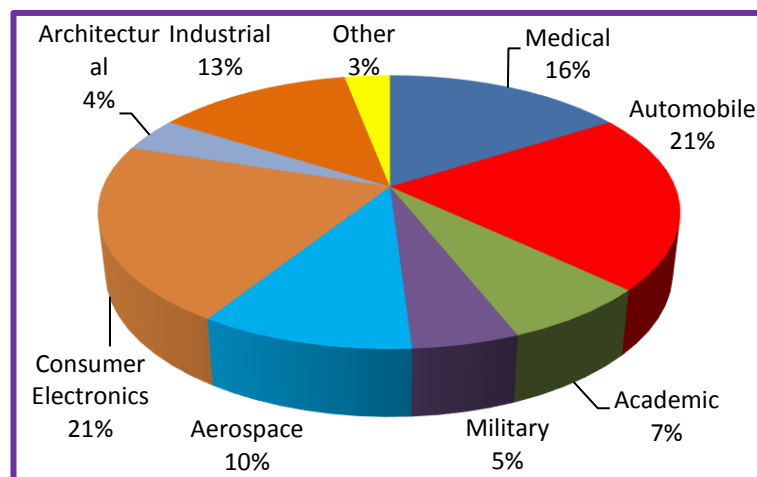


Figure 3: Revenue Split of AM Equipment Customers – 2012
(Royal Academy of Engineering, 2013).

3. Characteristics of Additive Manufacturing

3.1 Strengths

In Additive Manufacturing, time used for traditional trial-and-error process is significantly reduced so a new product can enter the market quickly. With AM technology, because no custom tooling is needed, the lead time in completing parts is greatly reduced. Due to its short build time, the technology is normally described as “rapid”, therefore, companies can promptly create a unique part that can replace a worn or broken one which can avoid costly or untimely shutdowns. In Additive Manufacturing, irrespective of part complexity, once a part is created as a CAD model, it can be printed. Using AM, storage of bulky patterns and tooling is virtually eliminated (www.additivemanufacturing.com, 2014; Pratt & Whitney, 2014).

3.1.1 Part Complexity

Since there is no tooling required in AM, internal features and surfaces which are complex are created directly when building the part. Also, any geometrical complexity of a part has little effect on build times, as opposed to the conventional manufacturing processes (Giannatsis, 2009). In conventional processes such as moulding and casting, complexity of part may not affect the cycle times, but can require several weeks in making the master pattern depending on the extent of part complexity. In machining, complex features directly affect the cycle time and may even require more expensive equipment, tooling and fixtures (Rosen, 2007).

3.1.2 Material Types

Additive Manufacturing technologies produce 3D parts by directing materials spatially in several possible ways: thermal, chemical, mechanical and/or optical. In thermal processes, the material is formed into an object after which it undergoes a thermal transition to maintain the shape. In chemical-based processes, the manufactured shape is maintained by a chemical reaction (often polymerization). Mechanical processes rely on the physical deposition of cells or materials, and in optical processes, cells or polymers are manipulated using light (Gibson et al., 2010).

Specifically, AM processes being able to produce parts in a variety of materials such as: plastics, metals, ceramics, composites, and even paper with properties similar to wood. Furthermore, some processes can build parts from multiple materials and distribute the material based on its location in the part (Gibson et al., 2010).

3.1.3 Low Volume Production - Advantage

Due to high initial costs on custom tooling and lengthy setup times for most conventional manufacturing processes, they are not very cost effective for low-volume productions. Additive Manufacturing supports low per-part costs for low volume productions in that it requires minimal setup time since it builds a part directly from the CAD model (Guo and Leu, 2013).

3.2 Weaknesses

3.2.1 Large Parts

AM processes require more time for a larger part in the X-Y plane and will require more layers to be built in the Z-direction for parts which are relatively tall (i.e. high in the Z direction). Hence, in AM, built times are largely dependent upon the part size, thereby making the processes best suited for relatively small parts. For casting and moulding processes, cycle times are characterised by part thickness and also for machining cycle times are dependent upon the material and part complexity. Manufacturing of large parts with AM processes is not cost effective because of the current high costs of material for these processes (Guo and Leu, 2013; Chua et al., 2010).

3.2.2 High Accuracy and Surface Finish

Additive Manufacturing cannot match the precision and finishes offered by machining, hence, parts produced by AM may require secondary operations depending on its intended use (Chua et al., 2010).

3.2.3 High-volume Production

Also, because per part cost of tooling at very large quantities becomes insignificant and cycle times remain shorter for moulding and casting, they (moulding and casting) are therefore preferred to Additive Manufacturing for high volume production (Chua et al, 2010; Hague et al., 2004).

3.2.4 Material Properties

Additive Manufacturing is limited to some individual material types and as a result, materials that offer certain desirable properties may not be available. The properties of the final part made by Additive Manufacturing methods may not also meet certain design requirements. Also, the current prices for materials used in additive processes are far greater than more commonly used materials for other processes (Chua et al., 2010; Hague et al., 2004).

4. Process Cycle of Additive Manufacturing

4.1 Modelling

The AM process starts with a digital three dimensional representation of the object to be manufactured. Object representation (Figure 4–stage 1) which has been generated by conventional CAD software or obtained from Laser Scanning, Computer Tomography (CT), Magnetic Resonance Imaging (MRI), or Mathematical Modeling software is stored in a Standard Tessellation Language (STL) file (Figure 4–stage 2) (Sreenivasan et al., 2010).

The STL file is then imported into slicing software (figure 4-stage 3) in which the three dimensional digital object is sliced into layers (Figure 4–stage 4) and oriented appropriately in order to define the best possible tool path for the printer (Figure 4–stage 5) which then creates the object (figure 4- stage 6) via selective placement of material (Campbell et al., 2011).

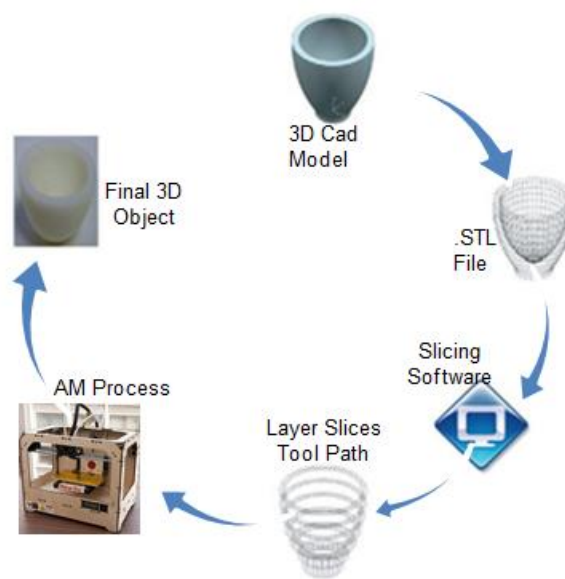


Figure 4: Additive Manufacturing Process Cycle

Additive Manufacturing takes information directly from Computer Aided Design (CAD) or animation modeling software and then slices them into digital cross-sections for the machine to successively use as a guideline for printing. Depending on the machine used, material or a binding material is deposited on the build bed or platform until material/binder layering is complete and the final 3D model has been "printed." It is a "What You See Is What You Get" (WYSIWYG) process where the virtual model and the physical model are identical (Guo and Leu, 2013).

Furthermore, it is important to select the appropriate building direction as this can determine specifications of the object such as cost, quality, and lead time. A direction chosen other than the optimum would lead to more layers required which will result in an increased lead time required to manufacture the product (Reeves, 2008).

4.2 Printing

When printing, the Additive Manufacturing machine first reads the design and then lays down layers of liquid, powder, or sheets of metal successively depending on the type of process by which way the model is built from series of cross sections. The final shape is created by joining together or automatically fusing together layers which corresponds to virtual cross section from CAD model. Most AM printers print a layer thickness of around 100 micrometres (0.1 mm), but some machines such as the *Objet Connex* series can print layers as thin as 16 micrometres

with the X-Y resolution comparable to that of laser printers. The particles (3D dots) are around 50 to 100 micrometres (0.05–0.1 mm) in diameter (Wohlers', 2005).

If a model is to be constructed with contemporary method several hours sometimes leading to several days depending on the method used and size and complexity would be needed. Additive systems can typically produce models in a few hours, although it can vary widely depending on the type of machine used as well as the size and number of models being produced simultaneously. Conventional process such as injection moulding can be less expensive for the manufacture of polymer products in high quantities, but Additive Manufacturing can be faster, more flexible and less expensive when producing relatively small quantities of parts. 3D printers give designers and concept development teams the ability to produce parts and concept models using a desktop size printer (Todd et al., 2005).

4.3 Finishing

The native resolution of a printer may be sufficient for some applications; if not, dimensional accuracy and surface finish can be enhanced by printing an object slightly oversized and then removing material with a higher-resolution subtractive process.

Some additive manufacturing techniques use two materials while constructing parts. The first material is the part material and the second is the support material (which supports overhang features during construction). The support material is later removed by heat or dissolved away with a solvent or water (Gibson et al., 2010).

5. Classification of Materials used in Additive Manufacturing

Additive Manufacturing Technologies are broadly classified in terms of material as: polymers, metals, ceramics, and composites. Some materials are applicable in more than one process whilst some processes also find themselves in many applications as shown in table 1 which summarizes the material groups, process(es) and specific material(s) applications.

Table 1: Classification of Materials Versus Corresponding AM Technologies/Techniques.

Material Group	AM Process(es)	Material(s)
Polymers	Thermo-setting	SLA, MJM
		Photo-curable polymers
		MJM
		Wax
	Thermo-plastic	SLS
Metals		Polyamide 12, GF polyamide, polystyrene
		FDM
		ABS, PC-ABS, PC, ULTEM
		3DP
		Acrylic plastics, wax
Ceramics		SLM
		Stainless steel GP1, PH1 and 17-4, cobalt chrome MP1, Ti6Al4V, Ti6Al4V ELI and TiCP, IN718, maraging steel MSI, AISi20Mg
		LDM/LENS
		Steel H13, 17-4 PH, PH 13-8 Mo, 304, 316 and 420, aluminium 4047, titanium TiCP, Ti-6-4, Ti-6-2-4-2 and Ti6-2-4-6, IN625, IN617, Cu-Ni alloy, cobalt satellite 21
		EBM
Composites		Ti6Al4V, Ti6Al4V ELI, cobalt chrome
		SLA
		Suspension of Zirconia, silica, alumina, or other ceramic particles in liquid resin
		FDM
		Alumina, PZT, Si ₃ N ₄ , zirconia, silica, bioceramic,
Uniform composites		SLS
		Alumina, zirconia, silica, ZrB ₂ , bioceramic, graphite, bioglass, and various sands
		3DP
		Zirconia, alumina silica, , Ti3SiC2, bioceramic, and various sands
		FDM
Functionally graded material (FGM)		Polymer-metal, polymer-ceramic, short fibre-reinforced composites
		3DP
		Polymer-matrix, metal-ceramic , short fibre-reinforced composites
		LOM
		Polymer-matrix, ceramic-matrix, fibre and particulate-reinforced composites
Metal-metal, metal-ceramic, ceramic-ceramic, polymer-matrix, short fibre-reinforced composites		SLS, SLM
		CoCrMo/Ti6Al4V, TiC/Ti, Ti/TiO ₂ , Ti6Al4V/IN718
		LMD/LENS
		PZT
		FDM
Al ₂ O ₃ /ZrO ₂		FEF

(Guo & Lee, 2013)

AM was initially used in similar applications of Rapid Prototyping and continuous research has resulted in a significant improvement in materials to be used from polymers to ceramics and metals and it is expected to be fully applied in full body organs by 2030 (www.raeng.org.uk, 2013). Figure 5 shows the development in AM where it was known as Rapid Prototyping together with future applications potential.

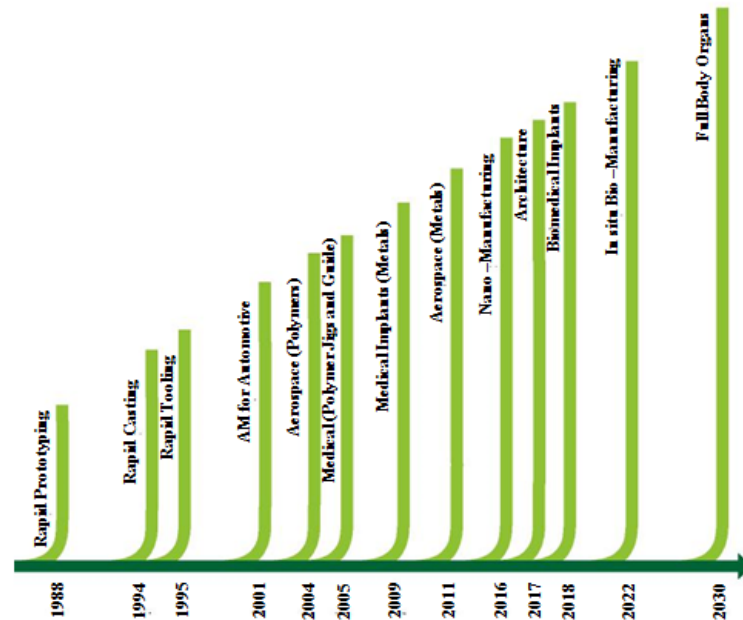


Figure 5: Additive Manufacturing Timeline from 1988 – 2030 (www.raeng.org.uk, 2013).

5.2 Medical Applications

Additive Manufacturing has gained grounds in the medical field even though there is more room for improvements. One opportunity is its use for medical devices for planning and conducting surgery and custom surgical implants (Christensen, 2013). Custom prosthetics and orthotics are other potential applications for AM which were relatively early uses of AM due to the ability to produce custom-fit parts for highly variable joints, amputated limbs, and cavities (for example, ears for hearing aids) (Melchels, 2012). What makes AM technologies even more appealing in medical applications is that they utilize medical imaging data obtained by Computer Tomography (CT) or Magnetic Resonance Imaging (MRI), almost directly for the production of customized patient specific parts (Giannatsis, 2009).

Using Additive Manufacturing for a custom implant offers several advantages such as making operation less complex, reducing operating time and the associated risk to the patient involved with being in surgery for so long. It also reduces the possibility of repeating a surgery that is needed because it cannot be done right the first time (Salmi et al., 2012; Giannatsis, 2002).

Figure 6 shows a model of 14-month's old child heart built in three pieces using a flexible filament printed at the School of Engineering at the University of Louisville. This took around 20 hours and cost US\$600. This allowed the doctors to better prepare for a successful operation (www.additivemanufacturing.com, 2014).

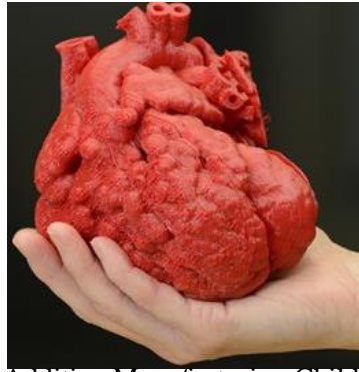


Figure 6: Additive Manufacturing Child Heart Model
(www.additivemanufacturing.com, 2014)

5.3 *Aerospace and Aeronautic Applications*

Additive Manufacturing is used for making non machinable complex parts for direct use preferably in the aerospace and the medical industry because of its mostly dense parts and very good mechanical properties (Gebhardt et al, 2010).

Aerospace and aeronautic components are critical parts which should be produced within very close tolerances to fulfil the high dimensional accuracy and surface finish. Also, when designing aerospace parts, producing of corners is avoided as much as possible to reduce stress concentration to the barest minimum and for this reason, critically chosen process should be used thereby making AM application more suitable (www.hk3dprinting.co.uk, 2013).

Additive Manufacturing technologies have proven to be a solution to parts complexities and therefore become the obvious choice for aerospace design as other forms of machining simply cannot meet the required standards. Also, often the case that the material required cannot be processed by conventional means and is too expensive in regards to buy-to-fly ratio are not relevant when it comes to Additive Manufacturing as the ratio is greatly reduced to minimize cost (www.hk3dprinting.co.uk, 2013). Figures 7 – 9 show examples of AM model aerospace parts.



Figure 7: Windform Tunnel Final Model (1:8 scale) for the Prototype of the Tilt Rotor
(www.additivemanufacturing.com, 2014).



Figure 8: AM Modelled Jet Engine
(www.additivemanufacturing.com, 2014)



Figure 9: AM Modelled Bladed Disk (Narine, 2007).

5.4 Tooling Applications

Figures 10 and 11 show sample of Additive Manufacturing or 3D printing used for the process of casting patterns for investment casting which is used to create a mould for use in metal casting.



Figure 10: Investment Casting Pattern (Pratt & Whitney, 2013).



Figure 11: 3D Systems CastForm PS Material Pattern (Pratt & Whitney, 2013).

5.5 Automotive Applications

Additive Manufacturing of automobile parts is a proven technology used by automobile engineers and designers to produce physical, tangible prototypes to work within design and testing. AM has been used to create a wide variety of parts in many materials, small and large automobile parts. Some examples of automobile parts produced by AM are Engine castings, engine parts, brakes, dashboards, handles, and knobs (www.protocam.com, 2014). Figures 12–15 show some automobile parts produced by AM technology.



Figure 12: AM Printed Turbocharger (www.protocam.com, 2014).



Figure 13: AM Printed Vehicle Brake (www.protocam.com, 2014).



Figure 14: Planetary Gearbox (www.grabcad.com, 2014).



Figure 15: Engine Block (www.grabcad.com, 2014)

6. Case Study at Northumbria University

6.1 Printed Skull

Figure 16 (1–3) shows a 3D printed skull at the Northumbria University 3D-Printing laboratory. The laboratory received the scanned data of the skull of the man in question who sustained a brain injury upon having a motor accident. The scanned data was saved in stl. file which was subsequently sent to the Objet 3D printing machine for printing. The figure 16 – stage 3 shows

the printed model which took approximately 20 hours to complete the printing. The printed skull clearly shows the damaged part.



Stage	Activity
1	CT Scan Model (.stl file)
2	Printed Model Halfway Cleaned
3	Final Printed Model

Figure 16: Printed Skull at Northumbria University

6.2 Some Parts Printed at Northumbria University

Figure 17 shows models for several applications printed at Northumbria University using various types of 3D facilities.



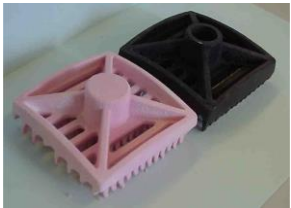
Nylon Bag (Z-Corps)



Mill (Z-Corps)



Duct (Z-Corps)



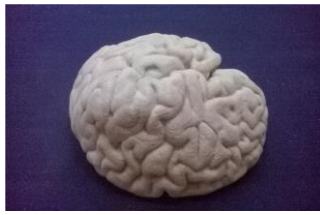
Square Hole Cutter (Z-Corps)



Millennium Bridge at
Newcastle upon Tyne
(Invasion Tech)



Auto Part
(Invasion Tech)



Human Brain
(Z-Corps)



Millennium Bridge at
Newcastle upon Tyne
(Z-Corps)



Northumbria University Logo
(3D Objet Printer)

Figure 17: Models Printed at Northumbria University

7. Conclusions and Future Work

7.1 Conclusions

Additive Manufacturing technology has a tremendous cost advantage when it is well understood and properly used. In Additive manufacturing, parts are precisely built by adding material layer by layer; hence, there is little or no waste of material as compared to traditional manufacturing where objects are created in a subtractive manner by trimming material (blank) and shaped to fit together properly. The problem of scrap disposal which is detrimental to the environment is eliminated and parts can be built on-site once the company can afford the machine and there is power supply. One of the major obstacles in Additive Manufacturing is surface finish which is critical to many engineering applications but not critical for most implants because coarse surfaces and porous structures are preferred as they favourably act as scaffolds for tissue growth (www.additivemanufacturing.com, 2013; Doubrovski et al., 2011; Karunakaran et al., 2013).

7.2 Future Work

The research team intends to look at conducting several tests on Polyurethane (PU) material to determine its suitability for Additive manufacturing technology applications for further reduction of weight and cost. The problem of surface finish is another issue the research team hopes to tackle by incorporating a system with the existing AM technology to match with other machining processes such as CNC machining and grinding.

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Effect of Varying Mixing Ratios and Pre-Heat Temperature on the Mechanical Properties of Polyurethane (PU) Foam

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Abstract

The continuous growth of the usage of Polyurethane foams requires that designers and manufacturers investigate the appropriate factors that affect their production and full usage in order to exploit their full potential. This research reports the effects of the mixing ratio of the main constituents (polyol and diisocyanate) which form the polyurethane foams and different pre-heat temperatures of the separate chemicals before mixing. The work has documented that there is a significant reduction of foaming time of 452 seconds at 20°C to 54 seconds at 100°C when the main constituents are pre-heated before mixing. Both tensile and compressive strengths are improved with increasing the ratio of diisocyanate to polyol. The density of the foam also increases when the concentration of polyol is increased.

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Keywords: Polyurethane Foam; Polyol; Diisocyanate; Mixing Ratios.

1. Introduction

Polyurethanes (PU's) are used in many applications, such as aeronautics (e.g. friction dampers), automobile (e.g. car dashboard), building construction (e.g. insulation purposes), marine (e.g. boat body), and many household applications (e.g. furniture) [1]. Their usage continues to grow as they can be used in areas where other materials do not work due to their lightweight stiff structure [2]. PU's are among the widely used construction materials that can be formulated for medical devices [2, 3]. Designers and manufacturers need to investigate the significant factors that affect their production and full usage in order to leverage these versatile properties [3, 4, 5]. PU's are polymers containing soft segment (polyol) and hard segment (diisocyanate) that are altered to control their structures and properties. The reaction between the diisocyanate and the chain extender produces the rigid, hard segments, whereas the soft segments are comprised of polyether, polyester or polycarbonate diol (polyol). The soft matrix is strengthened by the hard fields. The degree of phase separation which in turn affects the physical and mechanical properties [6], biocompatibility, and biodegradability [7] are influenced by the content of the hard segment [8]. The molecular weight of the main constituents of polyurethane (polyol and diisocyanate) and other segments can be varied to tune or modify these properties to serve in many areas

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such as in tissue engineering, either for reconstruction of soft tissue or for cartilage and bone generation [9]. One interesting application of PU is silicone implants containing a cohesive gel with the outside coated with polyurethane foam. When used as implants, PU's have the advantage of preventing capsular contracture and displacement or rotation of the implant thereby reducing re-operation in breast augmentation surgery [10]. Even though these implants coated with PU foams take about 3-6 months to soften, various articles have reported that they feel warmer and more like real breasts than other implants [11].

The processing of polyurethane foam requires certain chemicals and some aids such as blowing agents to ensure sufficient control to produce useful polyurethane foam required for commercial products. During the foaming process, a surfactant controls an interaction that takes place between the non-homogeneous components of the reacting system. In many cases, chain extenders or cross linkers, as well as fire retardants, fillers and pigments are used to modify the properties of the polymer structures [12]. Depending on the formulation, the catalysts and the application, the reaction is typically started within few seconds and completed in a few minutes. Within this time, it is essential to dispense the reacting liquid mixture into the mould and also to clean the combined 'mixing and dispensing' equipment ready for the operation. The exothermic chemical reaction is completed within the mould and the manufactured article can then be removed from the mould [13]. In addition to the effect of mixing ratio and the pre-heat temperature, manufacturing the polyurethanes requires various chemicals to control the polyurethane-foaming reactions and to create the right properties in the end-product. It has been researched and established that all practical polyurethane systems include some of the additives mentioned in Table 1. This study reports on the effects of varying mixing ratio and pre-heat temperatures of the main constituents (polyol and diisocyanate) on the mechanical properties of the polyurethane foam to make it suitable in applications such as for Additive Manufacturing also known as 3D Printing technology.

Nomenclature

AM	Additive Manufacturing
PU	Polyurethane
3D	Three Dimensional
EDX	Energy Dispersive X-ray analysis
SEM	Scanning Electron Microscope
ASTM	American Society for Testing and Materials

Table 1. Polyurethanes additives and their functions [13]

Additives	Reasons for use
Catalysts	To speed up the reaction between polyol and polyisocyanate
Cross-linking and chain-extending agents	To modify the structure of the polyurethane molecules and to provide mechanical reinforcement to improve physical properties (e.g. adding a polyisocyanate or polyol with more functional groups)
Blowing agents surfactants	To create polyurethane as a foam to control the bubble formation during the reaction and, hence, the cell structure of the foam
Pigments	To create coloured polyurethanes for identification and aesthetic reasons
Fillers	To improve properties such as stiffness and to reduce overall costs
Flame retardants	To reduce flammability of the end product
Smoke suppressants	To reduce the rate at which smoke is generated if the polyurethane is burnt
Plasticisers	To reduce the hardness of the product

2. Experimental Work/Methodology

Different densities and thicknesses of polyurethane skin are produced depending on the blowing agent and the concentration in the reacting mix, but in this research, only the main constituents (polyol referred to as part 'A' and diisocyanate referred to as part 'B' respectively) of polyurethane foam were considered for analysis (A:B). A mixing ratio of 1:1 (50:50) was used as a reference and varied in both directions for 9 screening tests which included 30:70, 35:65, 40:60, 45:55, 50:50, 55:45, 60:40, 65:35 and

70:30. Results obtained indicated that for mixing ratios of 60:40, 65:35 and 70:30 (Part A higher than 55), the foam formed was soft and dimensionally unstable and worsened with increasing part 'A'. In the other direction of the mixing ratio where part 'A' decreased whilst part 'B' increased (i.e. 45:55, 40:60, 35:65, and 30:70), a rise in the foam strength was obtained however, above 60% of part 'B', the obtained foam was brittle and could be crushed by hand force. This means that further increase of part 'B' (such as 20:80 and 10:90) will be far more brittle and weaker. It was therefore agreed to use only 45:55, 50:50 and 55:45 mixing ratios for further investigations and analysis. Furthermore, tests to evaluate the effect of pre-heating on the produced foam were conducted by using 50:50 mixing ratio. The constituents were pre-heated prior to mixing at several pre-heating temperature ranging from 20°C to 100°C at a step of 10°C. In each case the foam was cast and the outer skin removed to a depth of about 10mm to obtain a homogeneous part. Samples of the foams produced at 20°C with mixing ratios of 55:45; 50:50 and 45:55 were scanned using an FEI Quanta 200 Scanning Electron Microscope (SEM) in order to assess the micro-structure of these samples. This was repeated for the samples produced from 50:50 mixing ratio and pre-heat from 20°C to 100°C at intervals of 10°C.

Blocks of foam produced with different mixing ratios were cut to 150mm x 100mm x 100mm and weighed using a calibrated sensitive scale of readability and reproducibility of 0.001g and ± 0.003 g linearity, 3sec stabilization time and standard error of $\pm 0.5\%$. Whilst the 50:50 mixing ratio was maintained and the main constituents pre-heated and hand mixed uniformly, the time taken for each mixing ratio to complete foaming from the beginning of bubbling (nucleation) to the complete stoppage of foaming was recorded using a stop clock. This was carried out to evaluate the effect of pre-heat temperatures on the foaming time. Standard tensile specimen sizes were cut from the foam according to ASTM D3039 and then tested using an Instron E3000 with a 3kN load cell under a crosshead speed of 8 mm/min and $\pm 0.005\%$ load cell accuracy as shown in Fig. 1. Similarly for compression testing, blocks were cut to 40mm x 40mm x 40mm according to ASTM 3410M and then tested using the Instron-3382 with a 100kN load cell under a crosshead speed of 8 mm/min $\pm 0.2\%$, maximum resolution of 0.1N and a load measurement of $\pm 0.5\%$, see Fig. 2. For both compressive and tensile tests as well as foam weight and size measurements, three readings were obtained and the average was computed and used for analysis.

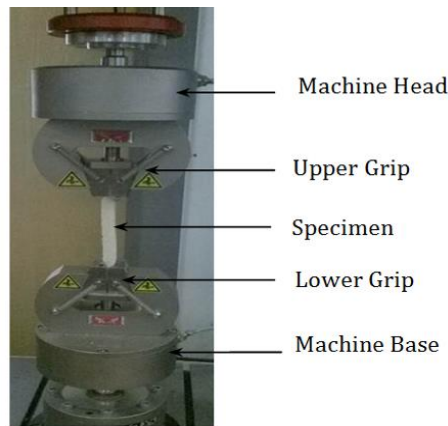


Fig. 1. Tensile testing using Instron E-3000

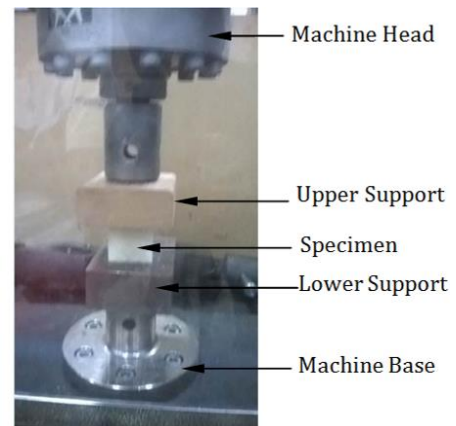


Fig. 2. Compressive testing using Instron 3382

The porosities of foam produced were determined using the liquid displacement method. In this method ethanol which penetrates into the pores of the foam was used as the displacement liquid. A specimen of each of the PU foam scaffolds produced was dried at room temperature and placed in a graduated cylinder which is filled with ethanol to an initial volume (V_1) and subjected under vacuum for 20 minutes for the ethanol to fill the pores of the scaffold. The volume (V_2) of the ethanol with the scaffold was noted. The scaffold was then removed from the ethanol and the remaining volume (V_3) was noted [12]. The percentage porosity 'P (%)' of the scaffold was then calculated as follows:

$$P(\%) = \frac{(V_1 - V_3)}{(V_2 - V_3)} \times 100 \quad P(\%) = \frac{(V_1 - V_3)}{(V_2 - V_3)} \times 100 \quad (1)$$

Where: $(V_2 - V_3)$ = total volume of the scaffold, and $(V_1 - V_3)$ = volume of ethanol retained in the scaffold sample.

3. Results and Discussions

3.1. Effect of varying mixing ratio on Polyurethane foam

Fig. 3 shows that the density of the PU foam increases with increasing part B (diisocyanate) of the PU main constituents and vice versa. Densities for the produced foam using different mixing ratios are presented in Table 2. The average density for the 55:45 mixing ratio was 46.2 kg/m^3 , and that obtained from 50:50 mixing ratio was 48.0 kg/m^3 , whilst that obtained for 45:55 mixing ratio was 53.3 kg/m^3 . The average density obtained from the 55:45 mixing ratio indicates a 3.8% reduction when compared to the density of the 50:50 mixing ratio whilst that obtained for the 45:55 mixing ratio indicates an 11% increase when compared to the result for the 50:50 mixing ratio.

Porosities for the produced foam using different mixing ratios are presented in Table 3. From the results obtained using the liquid displacement method to measure the porosity level, it could be observed that the 55:45 mixing ratio had the highest porosity of 43%. This was followed by the 50:50 mixing ratio with a porosity of 33% and then the 45:55 ratio which had the least porosity of 29% as plotted in Fig. 4. This must therefore be precisely controlled by adding other chemicals to obtain the required standard of foam for the desired purposes. When the porosity of the 55:45 mixing ratio was compared to that of the 50:50 mixing ratio a 30% increase was obtained. The 45:55 mixing ratio indicates a 12.1% decrease in porosity when compared to the density of the 50:50 mixing ratio.

Table 2. Densities of different mixing ratios

Mixing Ratio	55:45	50:50	45:55
Density (kg/m^3)	46.2	48.0	53.3

Table 3. Porosities for different mixing ratios

Mixing Ratio	55:45	50:50	45:55
Porosity (%)	43	33	29

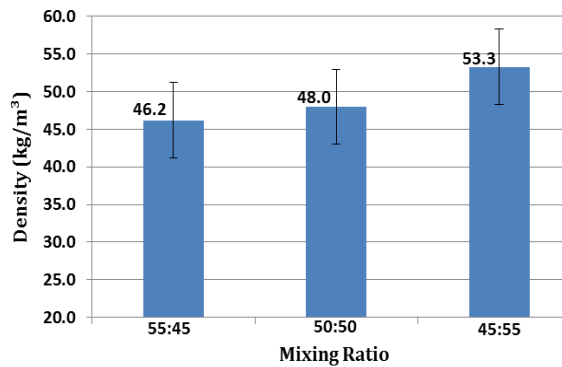


Fig. 3. Density results versus mixing ratios

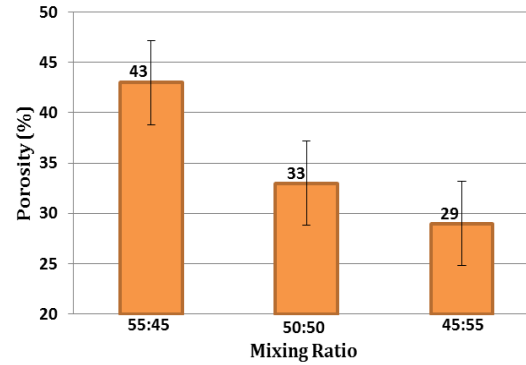


Fig. 4. Porosity results versus mixing ratios

The tensile stress-strain curves for the produced foams with varying mixing ratio are presented in Fig. 5. The results show that at the standard 50:50 mixing ratio, the tensile strength was 430.0kPa. This significantly increased to 516.6kPa when the mixing ratio was changed to 45:55 and reduced to 322.5kPa at mixing ratio of 55:45. This means the tensile strength of the PU foam was improved by 20.1% when the diisocyanate (part 'B') was increased from 50% to 55% mixing ratio and decreased by 33.3% when the polyol (part 'A') was increased from 50% to 55% of the mixing ratio. Unlike the tensile strengths which were quoted at just before failure, the compressive strengths were quoted at yield points. Fig. 6 shows that the maximum compressive stress is 240kPa for the 45:55 mixing ratio; followed by 185kPa for 50:50 mixing ratio and 148kPa for the 55:45 mixing ratio. This follows a similar trend to the tensile test results. When the 50:50 mixing ratio was used as reference, the compressive strength was increased by 30% when the diisocyanate was increased from 50% to 55% of the mixing ratio. This means that with

careful control, the compressive strength of the PU foam can be improved to suit a particular application by increasing the diisocyanate and vice versa if higher strain of the material is required.

Images obtained from SEM analysis (shown in Fig. 7) for mixing performed at 20°C showed that the 45:55 mixing ratio (Fig. 7c) has closer and better structured pores which makes it stronger than the 50:50 (Fig. 7b) and the 55:45 (Fig. 7a) mixing ratio foams. Even though the 55:45 mixing ratio also had closed pores, its dimensional stability is poor. Specimens cut out from the foam produced from 55:45 mixing ratio disfigured after 24 hours whilst that of 45:55 and 50:50 ratio foams of the same dimensions maintained their dimensional accuracy after the same period of time. This result suggests that beyond 50:50 mixing ratio which is the suppliers' recommendation, increasing the polyol decreases the dimensional stability as well as affecting the porosity and density of the polyurethane foam.

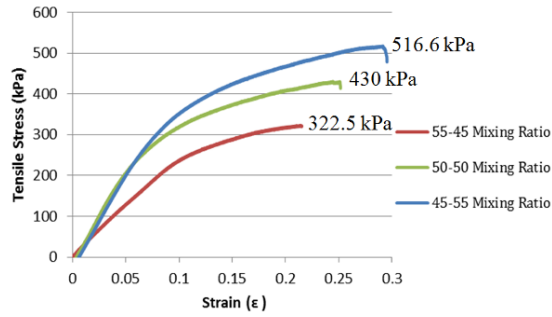


Fig. 5. Tensile stress strain curves for different mixing ratios

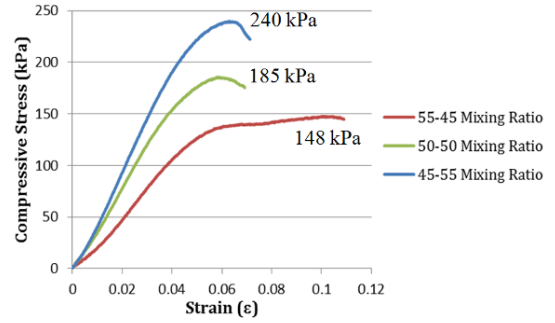


Fig. 6. Compressive stress strain curves for different mixing ratios

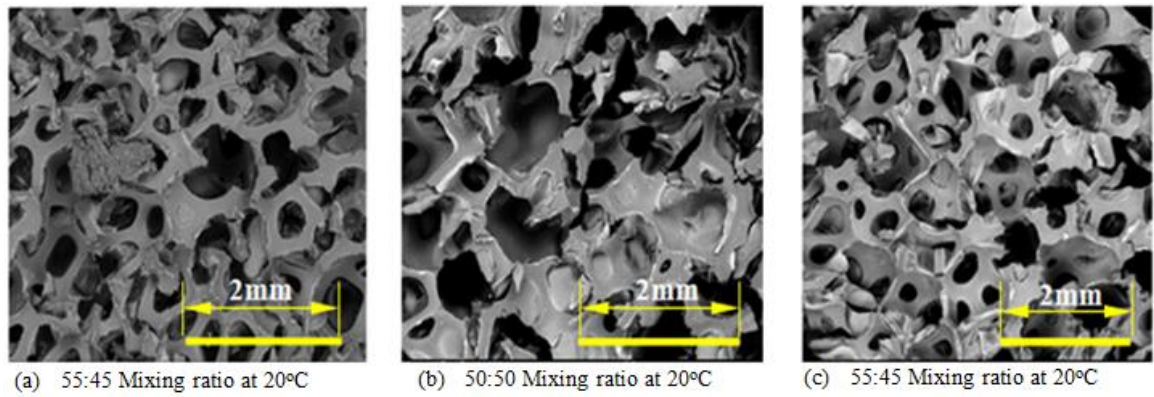


Fig. 7. SEM Images of PU Foam

3.2. Effect of pre-heat temperature on the produced foam

Results of foaming time versus pre-heat temperature are shown in Fig. 8. The results indicate that the foaming time at the standard temperature of 20°C was 452 seconds. This was reduced to 54 seconds at 100°C pre-heat temperature, indicating 88% reduction in foaming time. From the graph, there is a trend that the foaming time reduces as the pre-heat temperature increases, but the decrease in foaming time above 80°C pre-heat temperature is relatively insignificant.

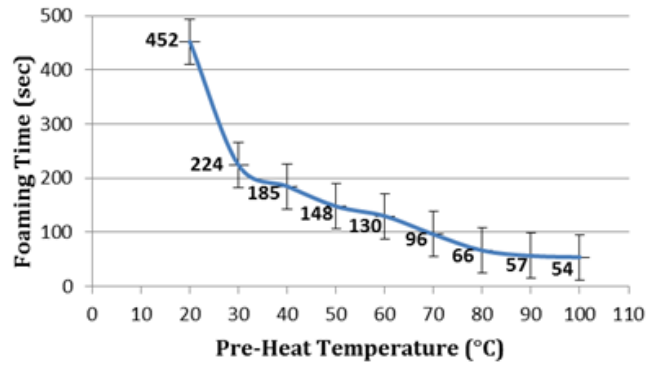


Fig. 8. Foaming time for different pre-heat temperature

The tensile stresses obtained for 50:50 mixing ratio foams, pre-heated from 20°C to 100°C are presented in Fig. 9. The 20°C pre-heat temperature had the highest tensile strength of 430kPa. This follows a reduction trend with increasing pre-heat temperature except the stresses at 70°C and 100°C pre-heat temperatures which were out of the trend. The least tensile stress recorded was 245kPa at 70°C pre-heat temperature. It could therefore be concluded that the tensile strength of the PU foam reduces with increasing foaming pre-heat temperature. Therefore, where the applications do not require much tensile strength and fall within the stated range of strength, the pre-heat would be of great advantage to significantly reduce foaming time which would make the PU material suitable for high speed process applications.

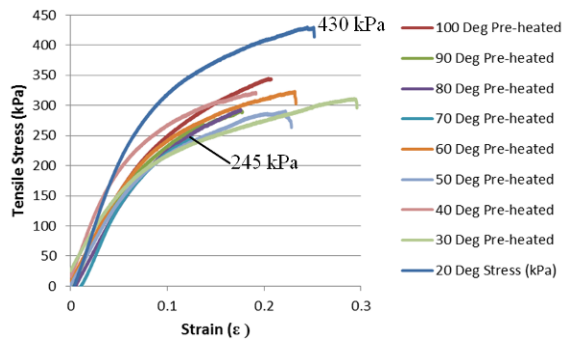


Fig. 9. Tensile stress results for foams produced at different pre-heat temperature

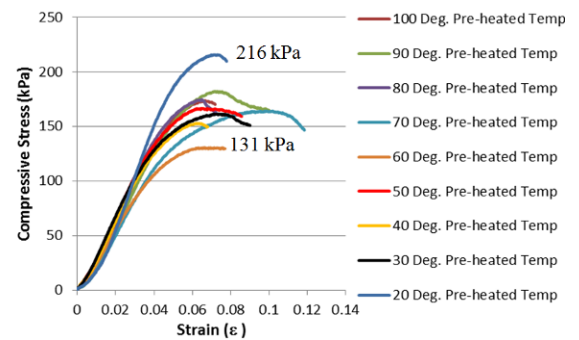


Fig. 10. Compressive stress results for foams produced at different pre-heat temperature

Fig. 10 shows compressive stress results for foams produced using 50:50 mixing ratio and at different pre-heat temperatures. The results indicate that foam produced with 20°C pre-heat temperature had the highest compressive stress (216kPa) compared with other pre-heat temperatures. When the pre-heat temperature is altered from 20°C, the compressive strengths do not have a consistent trend with the pre-heat temperature. The least compressive stress recorded was 131kPa for 60°C pre-heat temperature foam. Where compressive yield strength required for a particular application is not high, pre-heat temperature would be of great advantage. This can further be improved with the addition of other chemicals for higher compressive strength applications. The results obtained by maintaining the mixing ratio at 50:50 and varying the pre-heat from 20°C to 100°C at intervals of 10°C, show that the density decreases with increasing pre-heat temperature up to 60°C and increases with increasing pre-heat temperature beyond 60°C up to 100°C, as shown in Fig. 11.

Porosity results for PU foams produced using various pre-heat temperatures are shown in Fig. 12. From the results, it can be observed that the porosity increases from 33.3% at 20°C up to 45.2% at 60°C and decreases up to 37.3% at the earmarked 100°C. Even though this is not directly proportional to the density plot shown in Fig. 11, there is a trend which shows that the porosity increases with decreasing density and vice versa in relation to the pre-heat temperature as in Fig. 12. The increase of porosity from

20°C pre-heat temperature indicates a loss of strength when the temperatures of the PU chemicals were pre-heated before mixing.

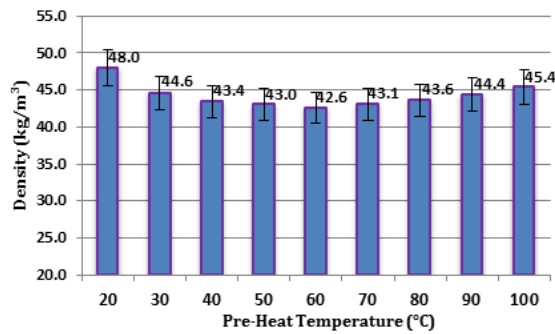


Fig. 11. Density of Different Pre-Heat Temperatures.

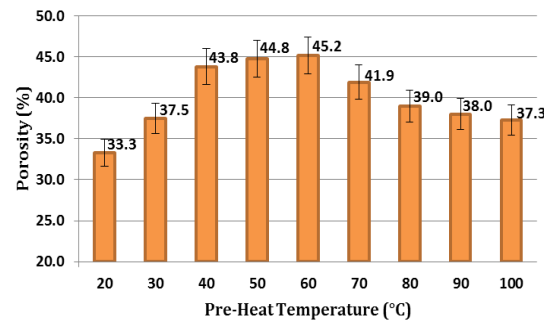


Fig. 12. Porosity of Different Pre-Heat Temperatures

The SEM images shown in Fig. 13 show that the scaffold structure of the 50:50 PU foam varies considerably with increasing pre-heat temperature. The results show that from 20°C to 40°C, the size of the pores of the foam increases which most likely corresponds to the increase of porosity and decrease of density. The pores of the 50°C specimen were marginally greater in size than the 40°C specimen but also slightly smaller in size than the 60°C specimen, also indicating an increase in porosity and a corresponding decrease in density. The pore size reduction continues until 100°C which indicates a decreasing trend of porosity and an increasing trend of density of the PU foam from 60°C pre-heat temperature to 100°C.

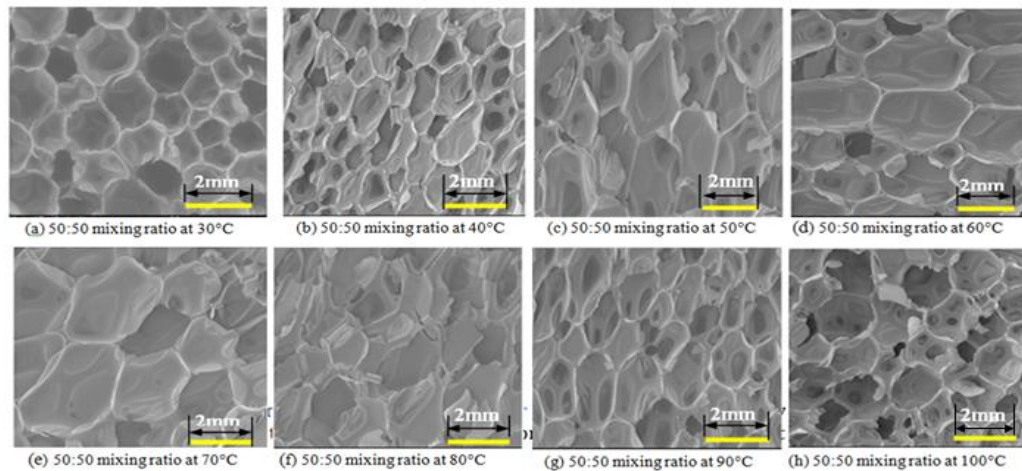


Fig. 13. SEM images of the PU foam produced at pre-heat temperatures from 30°C - 100°C

4. Conclusions

The results showed that varying the mixing ratio significantly affects the mechanical properties of the polyurethane foam. The measured tensile strength was improved with increased diisocyanate which is referred to as 45:50 mixing ratio and can further be improved with the addition of other chemicals depending on the intended application. The produced PU foams were found to have lower compressive strengths compared to the tensile strengths. These were only measured up to the yield point and also exhibited a similar trend as the tensile strengths. The variation of density was found to be very small. Increasing the pre-heat temperature resulted in a dramatic reduction of foaming time from 452 seconds at 20°C to 54 seconds at 100°C. It can be also concluded that there is significant effect on the mechanical and other properties such as foaming rate of polyurethane foam when the mixing ratio and pre-heat temperature of the main constituents are altered. The soft matrix is strengthened thereby improving the mechanical properties when the diisocyanate increases and the foaming rate improved with increasing

pre-heat temperature. These variations make the PU foam suitable for fast build time technologies such as 3D Printing for soft matrix scaffold, provided the properties due to the effects of the pre-heat temperature and mixing ratio variations are within the acceptable range for its intended purpose. There is also potential to further enhance the properties of these PU foams by adding one or more of the additives detailed in Table 1.

Acknowledgements

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C1.3 Conference on Rapid Design, Prototyping and Manufacturing (CRDPM) - 2015

Effect of Varying Mixing Ratios and Foaming Direction on Polyurethane Foam for Additive Manufacturing Applications

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ABSTRACT

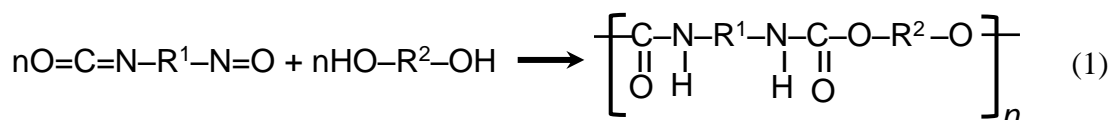
Polyurethane (PU) belongs to class of polymers that display thermoplastic, elastomeric, and thermoset behaviour depending on their chemical and morphological makeup. PU's biodegradability, biocompatibility, lightweight, and durability make it applicable to medicine such as implants. PU is usually produced in blocks of foam by casting in open-topped moulds, or other suitable enclosures, and machined to obtain the final shape and size. This paper analyses the effect of varying mixing ratios by volume on the tensile and compressive strengths for different foaming directions, and proposes an Additive Manufacturing system to dispense polyurethane foam for lightweight medical implant scaffolds. Results obtained indicate that the microstructures, tensile and compressive strengths differ in foaming directions. A concept has been proofed by spraying PU resins under pressure from two separate nozzles to foam on a surface which can be incorporated on an AM machine to dispense foam for applications such silicone gel breast implants.

KEYWORDS: Polyurethane, diisocyanate, polyol, biocompatibility, biodegradability, Additive manufacturing

1 INTRODUCTION

Polyurethane (PU) is a polymeric material belonging to a class of polymers that display thermoplastic, elastomeric, and thermoset behaviour depending on their chemical and morphological makeup [1]. PU's are versatile because of their unique chemistry and have soft segments that provide flexibility and hard segments that provide strength [1]. Polyurethanes are compact, and foamed variations in particular are very widespread, and they achieve their targeted properties at very low weights [2].

Polyurethanes are made by exothermic reactions between alcohols with two or more reactive hydroxyl (-OH) groups per molecule (diols, polyol, triols), isocyanates that have more than one reactive group (-NCO) per molecule (diisocyanate, polyisocyanates), catalysts, auxiliary blowing agents, and other additives to allow the resulting foam to rise freely. Equation 1 is an example of diisocyanate reaction with diol [1].



1.1 Polyurethane Applications

Because of the wide range of polyols and variety of diisocyanates used to produce PU, a broad spectrum of materials can be obtained to meet the needs of wider applications in diverse sectors. Their durability and lightweight, combined with their strength make them very versatile and they can be used in areas where other materials do not work [3, 4]. The material is therefore used in many applications, such as aeronautics (e.g. friction dampers), automobile (e.g. car dashboard, arm rests, bushings, etc.), building construction (e.g. insulation purposes), marine (e.g. boat body), and many household applications (e.g. furniture, footwear, etc.) [5]. PU's are also one of the most widely used structure materials for formulating medical devices [3, 6]. Designers and manufacturers need to investigate the significant factors that affect their production and full usage in order to influence these versatile properties. Table 1 shows some of the specific applications and properties of PU.

Applications	Properties
Cushioning	Low density, flexibility, resistance to fatigue
Shoe soles	Flexibility, resistance to abrasion, strength, durability
Building panels	Thermal insulation, strength, long life
Artificial heart valves	Flexibility and biostability
Electrical equipment	Electrical insulation, toughness, resistance to oils
Medical implants	Tough, biocompatible, biodegradable, and hemocompatible

Table 4: Specific applications and properties of PU's [1]

1.2 Silicone Gel Breast Implant

The polyurethane foam cohesive silicone gel breast implant is made from cohesive silicone gel contained in a low-bleed, barrier-type silicone elastomer shell, which is thin and soft and coated with a PU foam surface [7]. The cohesive gel fill aids the shape retention characteristics of the implants, making them feel soft and natural. The Silimed breast implants which are the most common brand available are made in a wide variety of shapes, sizes and projections, including the popular tear drop shape, see Figure 1. The PU coating is vulcanized to the elastomer shell of the implant [7].



Figure 1: Polyurethane foam cohesive silicone gel breast implants in varying sizes [7].

1.3 Additive Manufacturing Medical Application

Additive manufacturing (AM) is a technology that provides an alternative to traditional manufacturing methods. It is used to manufacture personalised products, enable supply chain compression, and cost reduction [8]. AM techniques offer the potential to fabricate organized tissue constructs to repair or replace damaged or diseased human tissues and organs [9]. Even though AM technology has been used in many medical applications [10], it has not been used to produced PU foam for medical applications due to the foaming nature of the material.

2 EXPERIMENTAL WORK/METHODOLOGY

2.1 Production of PU

The production of Polyurethanes is achieved by mixing two or more liquid streams. These two components are denoted as the polyurethane system [11]. The two main streams are: 1) polyol stream which is referred to as “Part A” or just ‘poly’ and 2) isocyanate which is commonly referred to as ‘Part B’ or just the ‘iso’. This mixture might also be called a ‘resin’ or ‘resin blend’. Resin blend additives may include chain extenders, cross linkers, surfactants, flame retardants, blowing agents, pigments, and fillers which are normally contained in the polyol stream. Polyurethane can be made in a variety of densities and hardness by varying the isocyanate, polyol, or additives. For consistency, this paper refers to Polyols as “Part A” and isocyanate or otherwise diisocyanate as “Part B” and bases its analysis on these two constituents.

Depending on the formulation, the catalysts and the application, the reaction is typically started within a few seconds and completed in a few minutes [12]. Within this time, it is essential to dispense the reacting liquid mixture into the mould and also to clean the combined ‘mixing and dispensing’ equipment for the next cycle [5]. The exothermic chemical reaction is completed within the mould and the manufactured article can then be removed from the mould. Most PU foams are manufactured using continuous processing technology and can be produced in batches where relatively small blocks of foam are made in open-topped moulds, boxes, or other suitable enclosures. The obtained foam block is cut to the required shape and size for its intended purpose by any conventional machining process such as CNC machining [13].

The mixing ratios considered for this research is as illustrated in table were 40:60, 45:55, 50:50, and 55:45, Part A:B. The 50:50 mixing ratio was used as the reference as many researchers have used that with varying additives to suit their requirements. Part A was increased to 70% and Part B decreased to 30%, both at intervals of 5% and

decreased to 40% with part B increased to 60%, also at intervals of 5%. Therefore, the total mixing ratio considered for the screening test was 9, as illustrated in table 2.

Part A (%)	70	65	60	55	50	45	40	35	30
Part B (%)	30	35	40	45	50	55	60	65	70

Table 2: Mixing Ratio for Screening Tests

Moulds of size 200mm x 200mm x 200mm were used for the casting in order that full dimensions of specimen could be obtained in both free foaming directions along the open top and restricted foaming direction against the walls of the mould. The outer skins of the produced foams were removed to a depth of about 10mm to obtain a homogeneous part.

Once the foam specimens were prepared, an initial screening test was conducted to reveal the key mechanical property attributes and/or inadequacies in the material system candidates. The results obtained from the screening test indicated that when the fraction of Part A was higher than 55% (i.e. 60:40, 65:35 and 70:30), the foam obtained was soft and disfigured after curing. Conversely, when the fraction of Part B was higher than 60% (i.e. 35:65 and 30:70) the obtained foam was brittle and could be crushed by hand force. This suggested that further increasing the fraction of Part ‘B’ (such as 25:75 and 20:80) would produce foams that were even more brittle and weaker. It was therefore agreed to use only 40:60, 45:55, 50:50 and 55:45 mixing ratios for further investigations and analysis.

Standard tensile specimen sizes were cut from the foam according to ASTM D3039 and then tested using an Instron E3000 with a 3kN load cell under a crosshead speed of 8 mm/min and $\pm 0.005\%$ load cell accuracy. Similarly for compression testing, blocks were cut to 40mm x 40mm x 40mm according to ASTM 3410M and then tested using the Instron-3382 with a 100kN load cell under a crosshead speed of 8 mm/min $\pm 0.2\%$, maximum resolution of 0.1N and a load measurement of $\pm 0.5\%$. For both tensile and compressive tests, three samples were tested in both x and y axes and the average of the readings obtained were used for analysis. Images of the microstructure of the foam samples were obtained using FEI Quanta 200 Scanning Electron Microscope (SEM) in both free foaming and restricted foaming directions.

2.2 Dispensing of PU using airbrushes – proof of concept

Two airbrushes, each containing one of the two resins (polyol, diisocyanate), were used to supply the liquids which were pre-heated to 40°C in the form of spray for easy mixing by the influence of compressed air which was supplied at 1.5 bar. The air brushes were inclined at 30° and kept a distance away such that the two liquids converged at the point of deposition.



a) TC 2000 Compressor set-up

b) Dispensing unit in holder

Figure 3: Proposed AM attachment for dispensing of polyurethane foam

3 RESULTS AND DISCUSSION

The images obtained from the SEM (Figure 4) for the 4 mixing ratios considered were captured at the same scale for fair and accurate comparisons. It can be clearly seen that there is distinction between the structures in the restricted (foaming against the mould walls) foaming direction and that in the free foaming directions. The microstructures of the foams in the free foaming direction are more compact and well arranged than those in the restricted foaming direction. For example the microstructures of the 40:60 and 45:55 foams looks more compact in the free foaming direction than in the restricted foaming direction. The 50:50 and the 55:45 mixings ratios exhibited the same characteristics.

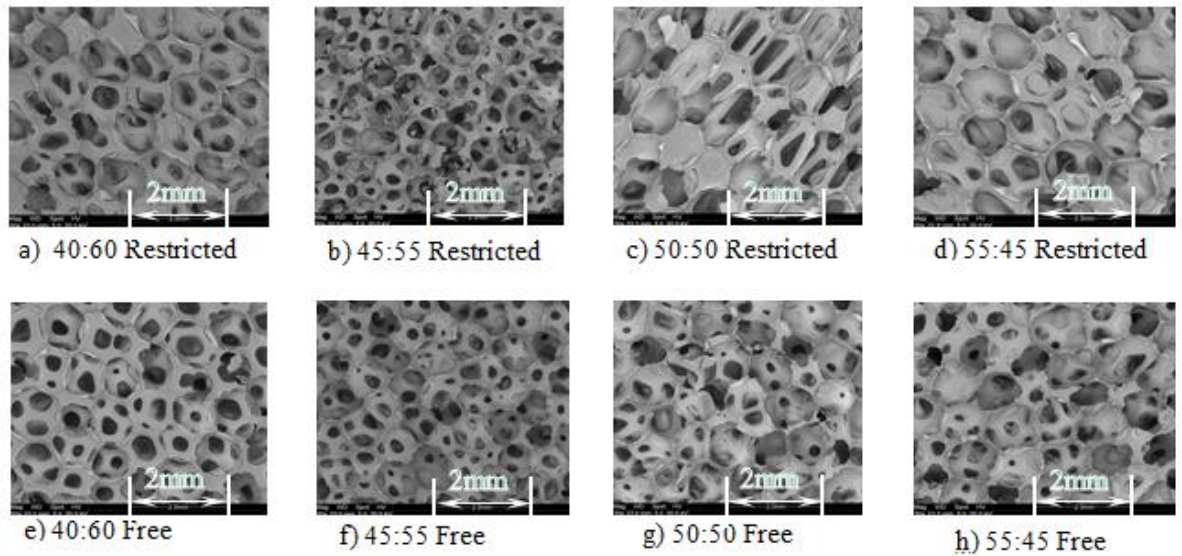


Figure 4: SEM Images of PU

From the results obtained from the tensile testing (figure 5 and figure 6), the average tensile strength obtained for 40:60 mixing ratio in the restricted foaming direction was 590 kPa whilst that obtained in the free foaming direction was 834 kPa. The free foaming direction therefore indicates a 41% increase in strength when compared to the restricted foaming direction. The average tensile strength for the 45:55 mixing ratio in the restricted foaming direction was 496 kPa whilst that in the free foaming direction

was 912 kPa, indicating a 45.6% increase in tensile strength. The average tensile strength for the 50:50 mixing ratio in the restricted foaming direction was 353 kPa whilst that obtained in the free foaming direction was 626 kPa, giving an average increase in tensile strength of 77%. The average tensile strength for the 55:45 mixing ratio in the restricted foaming direction was 345 kPa whilst that in the free foaming direction was 578 kPa, indicating an average increase in tensile strength of 67.5%. Therefore, using the 50:50 (50% polyol and 50% diisocyanate respectively) mixing ratio as the reference, it could be realised that the tensile strength was increased when the percentage of diisocyanate was increased to 55% with the polyol decreased to 45% (45:55 mixing ratio). However, as the diisocyanate was increased to 60% and the polyol was decreased to 40%, even though the tensile strength was more than the 50:50 mixing ratio, it was less than that of the 45:55 mixing ratio.

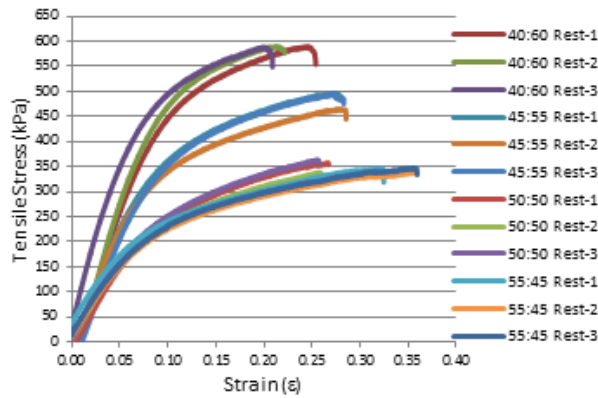


Figure 5 Tensile stresses of PU for restricted foaming direction

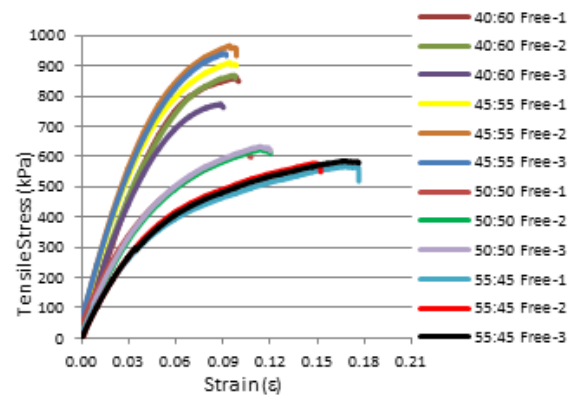


Figure 6 Tensile stresses of PU for free foaming direction

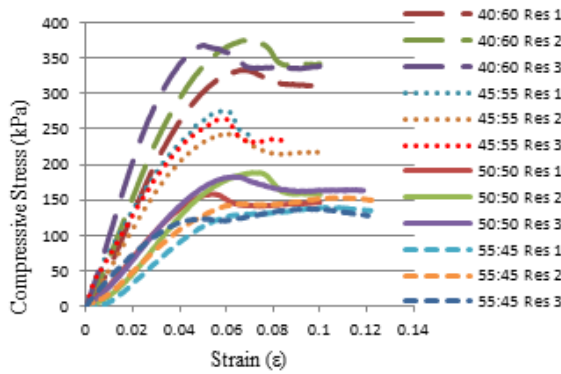


Figure 7 Compressive stresses of PU for restricted foaming direction

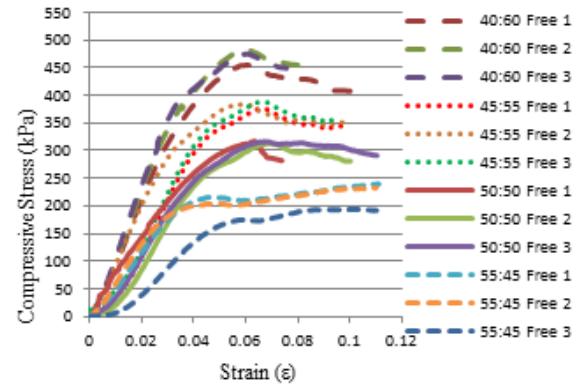


Figure 8 Compressive stresses of PU for free foaming direction

The strength of the foams in compression was measured up to the yield point. The results obtained for the compressive stresses in the restricted and free foaming directions are plotted in figure 7 and figure 8 respectively. From the results the average compressive strength for the 40:60 mixing ratio in the restricted foaming direction was 360 kPa whilst that for the free foaming direction was 470 kPa, yielding a 30.6% increase in compressive strength. The average compressive strength for the 45:55 mixing ratio in the restricted foaming direction was 262 kPa whilst that obtained for the

free foaming direction was 388 kPa, indicating 48% increase in strength. The compressive yield stress for 50:50 mixing ratio was 176 kPa in the restricted foaming direction and that in the free foaming direction was 315 kPa, indicating 80% increase in compressive strength. The average compressive strength for the 55:45 mixing ratio in the restricted foaming direction was 144 kPa whilst that in the free foaming direction was 205 kPa, which is 42.4% increase in compressive strength. The results obtained for the compressive stresses indicated that the strength of the 45:55 mixing ratio was more than that of the 50:50 mixing ratio and that of the 55:45 mixing ratio was less than that of the 50:50 mixing ratio. Unlike the tensile strengths, the average compressive strength of the 40:60 mixing ratio was more than that of the 45:55 mixing ratio.

Figures 9 and 10 show the results obtained when the proposed system was used to dispense the PU resins from separate reservoirs to foam on the application surface. The foamed depth was measured using a depth guage and it was found to be 2.5 mm minimum and 3.5 mm maximum.



Figures 10 Some cured PU foam images produced using the proposed system

Table 3 illustrates the summary of the results obtained for the tensile and compressive stresses for both restricted and foaming directions with their respective strains.

Mixing Ratio	40:60		45:55		50:50		55:45	
Foaming direction	Restricted	Free	Restricted	Free	Restricted	Free	Restricted	Free
Tensile Strength (kPa)	590	834	486	940	353	626	345	578
Strain	0.220	0.095	0.275	0.093	0.250	0.111	0.344	0.162
Compressive Strength (kPa)	360	470	261	389	177	315	144	205
Strain	0.063	0.061	0.060	0.062	0.064	0.067	0.1.2	0.298

Table 3 Summary of Tensile and Compressive Results for Restricted and Foaming Directions.

4 CONCLUSIONS

It has been shown that the microstructure of the same PU foam cast is different depending on the foaming direction. It was realised from the analysis that both compressive and tensile strength of the PU foam is higher in the free foaming direction compared to the restricted foaming direction (foaming direction against the walls of the mould). The compressive strength of the PU foam increases by increasing the fraction of Part B (diisocyanate) up to 60%, but beyond this value the foam becomes brittle and its usefulness reduces. The tensile strength of the foam increases with increasing percentage of Part B. However, above 55% of Part B, the tensile strength begins to reduce. It can therefore be concluded that because the PU foam is anisotropic, the foaming direction should be taken into consideration in its application. Though the strength can be increased by increasing the fraction of the diisocyanate, Part B, it should not be increased beyond 55% when under tensile load, or 60% when under compressive load.

Polyurethane resins can be mixed outside a chamber under compressed air to foam. A more volumetric foam can be obtained by repeating layers. The proposed system can therefore be attached to the 3D printer controls to dispense polyurethane according to the stl file supplied to the system.

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C1.4 Rapid Design, Prototyping and Manufacturing Journal – Under Review

Additive Manufacturing: Past, Current, and Future Development

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ABSTRACT

Additive Manufacturing which is the official industry standard term (ASTM 2792) for all applications of the technology encompasses many processes such as: Additive Fabrication, Rapid Prototyping, 3-Dimensional Printing, Layer Manufacturing, and Solid Freeform Fabrication. The technology is dignified to bring revolt in the manufacturing sector; regarding product design, production, and final distribution to the end user. Each of these stages in manufacturing sector could be modified and improved to bring cost reduction in final product to the user.

The technology that was started about three decades ago as rapid prototyping solutions has gone through a lot of developments and further expected to produce full body organ by 2030. This paper reviews the past, current and future development of the AM technology.

KEYWORDS: Additive Manufacturing, Additive Fabrication, Rapid Prototyping, Conventional Machining,

INTRODUCTION

Additive Manufacturing (AM) which is the official industry standard term (ASTM 2792) for all applications of the technology encompasses many processes such as: Additive Fabrication (AF), Rapid Prototyping (RP), 3-Dimensional Printing (3DP), Layer Manufacturing (LM), and Solid Freeform Fabrication (SFF)[1]. The technology is dignified to bring revolt in the manufacturing sector, regarding product design, production, and distribution to the end user. The technology differs from the

conventional machining techniques where material is removed incrementally until the desired shape or dimensions are achieved, in that it is a layer- by-layer technique of producing three dimensional solids generated directly from 3-D model data in which one layer is formed atop the previous one until the required geometry or shape is obtained. Whilst subtractive processes start from the top down, additive processes start from the ground up[2].

When AM is fully understood and utilised correctly, an impressive niche and cost saving are possible. Parts and devices that are geometrically complex and have graded material compositions which otherwise are impossible to fabricate by conventional method as a whole can now be fabricated by AM technologies as a single customised component[3]. The technology has tremendously helped trim weeks, even months of design, prototyping and manufacturing time whilst avoiding costly errors and improving product quality.

2 Characteristics of Additive Manufacturing

2.1 Strengths

Many of the Traditional Manufacturing processes require trial-and-error to accomplish the final product, thereby causing delay for new product to enter the market. Since no custom tooling is needed for AM technology, the lead time required to complete parts is significantly reduced. The technology is sometimes described as ‘rapid’ due to its short build time, enabling companies to promptly create a unique part that can replace a worn or broken one which can avoid costly or untimely shutdowns. In Additive Manufacturing, irrespective of part complexity, once a part is created as a CAD model, it can be printed. Using AM, storage of bulky patterns and tooling is virtually eliminated[4]. AM supports low per-part costs for low volume productions in that it requires minimal setup time since it builds a part directly from the CAD model[5].

The non-requirement of tooling for AM enables internal features and surfaces which are complex to be created directly. Also, any geometrical complexity of a part has little or no effect on build times, as opposed to the conventional manufacturing processes[6]. Even though in certain conventional technologies such as moulding and casting, complexity of part may not affect the cycle times, several weeks may be required in making the master pattern depending on the extent of part complexity. In machining, complex features directly affect the cycle time and may even require more expensive equipment, tooling and fixtures[7].

Additive Manufacturing technologies produce 3D parts by directing materials spatially in several possible ways: thermal, chemical, mechanical and/or optical. In thermal processes, the material is formed into an object after which it undergoes a thermal transition to maintain the shape. In chemical-based processes, the manufactured shape is maintained by a chemical reaction (often polymerization)[8]. Mechanical processes rely on the physical deposition of cells or materials, and in optical processes, cells or polymers are manipulated using light[8].

Specifically, AM processes are able to produce parts in a variety of materials such as: plastics, metals, ceramics, composites, and even paper with properties similar to wood. Furthermore, some processes can build parts from multiple materials and distribute the material based on its location in the part[8].

Whilst subtractive processes such as milling, turning, etc., start from top down, AM processes start from the ground top by building the part layer-by-layer. This avoids waste or cost in recycling of scrap or environmental pollution by scrapping as shown in Figure 1.

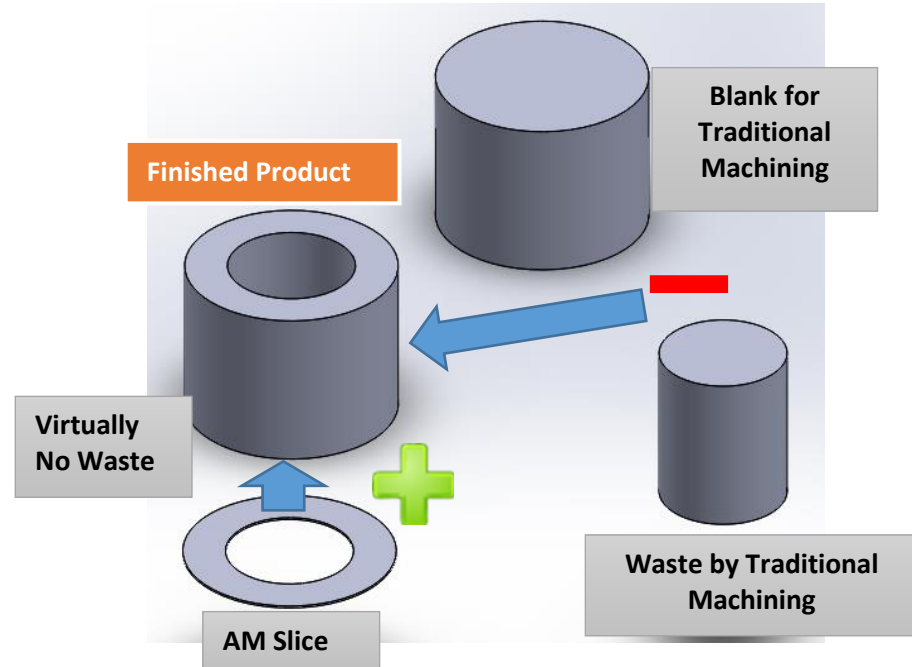


Figure 1: Waste Comparison of Additive Manufacturing and Conventional Machining

2.2 Weaknesses

AM processes require more time for a larger part in the X-Y plane and will require more layers to be built in the Z-direction for parts which are relatively tall (i.e. high in the Z direction)[5]. Hence, in AM, built times are largely dependent upon the part size, thereby making the processes best suited for relatively small parts[1]. For casting and moulding processes, cycle times are characterised by part thickness and also for machining cycle times are dependent upon the material and part complexity. Manufacturing of large parts with AM processes is not cost effective because of the current high costs of material for these processes[1, 5].

The precision and finishes offered by machining cannot be matched by AM, hence, parts produced by AM may require secondary operations depending on its intended use[1].

Also, because per part cost of tooling at very large quantities becomes insignificant and cycle times remain shorter for moulding and casting, they (moulding and casting) are therefore preferred to Additive Manufacturing for high volume production[1, 9].

Additive Manufacturing is limited to some individual material types and as a result, materials that offer certain desirable properties may not be available. The properties of the final part made by Additive Manufacturing methods may not also meet certain design requirements. As well, the current prices for materials used in additive processes are far greater than more commonly used materials for other processes[1, 9].

3 Additive Manufacturing Technology Advancements

3.1 Industry Growth

Figure 2 shows the percentage of cumulative industrial additive manufacturing systems installed in various countries from 1988 to 2012. Whereas the U.S. continued to lead by a large margin, Japan, Germany, and China followed as second, third, and fourth respectively as the largest installed bases[10].

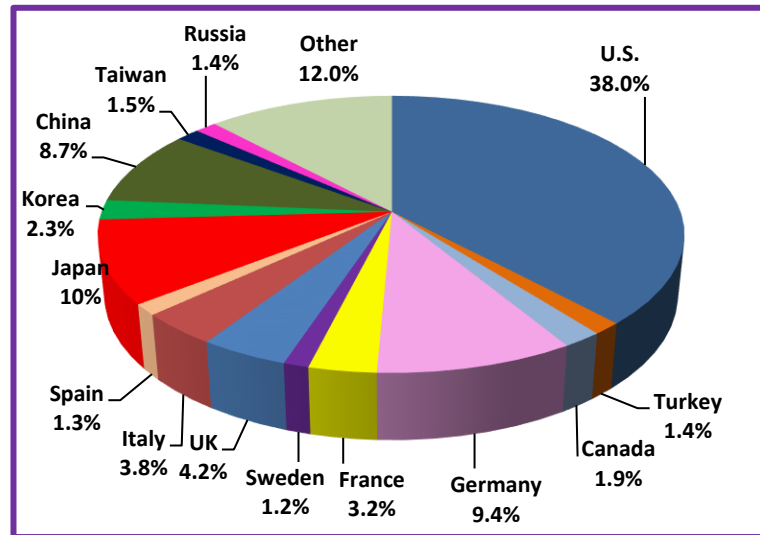


Figure 2: Countries Participation in Additive Manufacturing from 1988–2012 [10]

3.2. Additive Systems Manufacturers

The demand for products and services from Additive Manufacturing technology keeps on increasing from time to time. Therefore, system manufacturers of AM are striving to meet the demand of users in various categories. Thirty five manufacturers from different parts of the world produced and sold AM systems in 2009 as against 34 in 2008. Figure 3 shows the 2009 unit sales market shares among manufacturers worldwide[11].

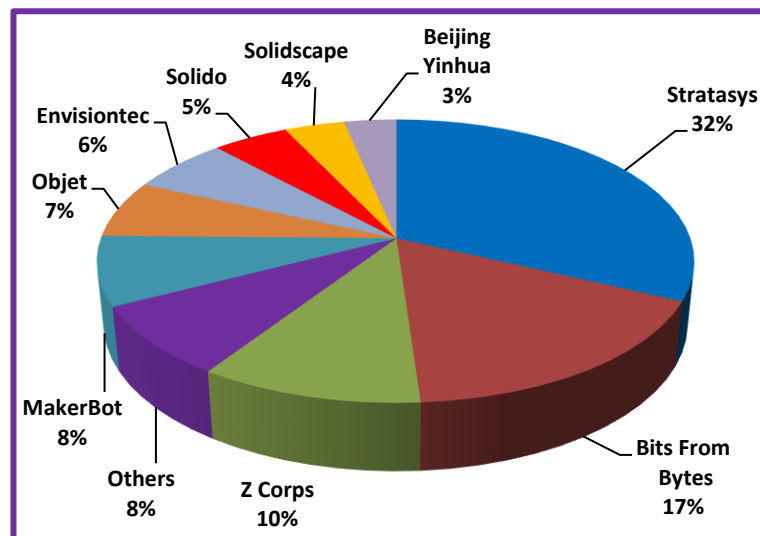


Figure 3: Additive Systems Manufacturers Worldwide [10]

3.3 Revenue Split of AM Equipment Customers - 2012

According to Wohlers report[12], it is observed from the chart (Figure 4) that Automobile and Consumer Electronics both led with 21% each of the overall revenues by Additive Manufacturing technologies. The Medical sector contributed 16% which puts them behind only Automobile and Consumer Electronics, both being key users of the AM technology. However, the main difference between them is that Medical industry uses the AM technology for direct production of products, whereas, the others use it primarily for prototyping purposes [12].

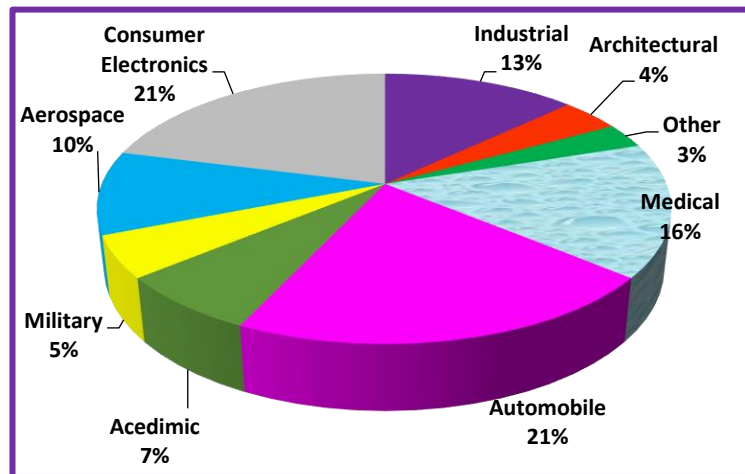


Figure 4: Revenue Split of AM Equipment Customers -2012 [10]

4 Future of Additive Manufacturing

4.1 Expected Growth of Additive Technology

Over a period of half decade, applications for Additive Manufacturing have been developed by many industries and researchers strive to discover more of its applications[12]. The advantages of the technology have been embraced and exploited by many industries such as: aerospace, automotive, medical, jewellery, architectural, etc. The services and products of Additive Manufacturing worldwide were predicted in 2013 for 2015–2021 as illustrated in the Table 1[12].

Table 1: Expected Growth of Additive Manufacturing

Predicted Year	Total Estimate (£)
2015	2.8 billion
2017	4.3 billion
2021	7.7 billion

4.2 Development of Additive Manufacturing

AM was initially used in similar applications of Rapid Prototyping and continuous research has resulted in a significant improvement in materials to be used from polymers to ceramics and metals and it is expected to be fully applied in full body organs by 2030[12]. Figure 5[12] shows the development in AM where it was known as Rapid Prototyping together with future applications potential.

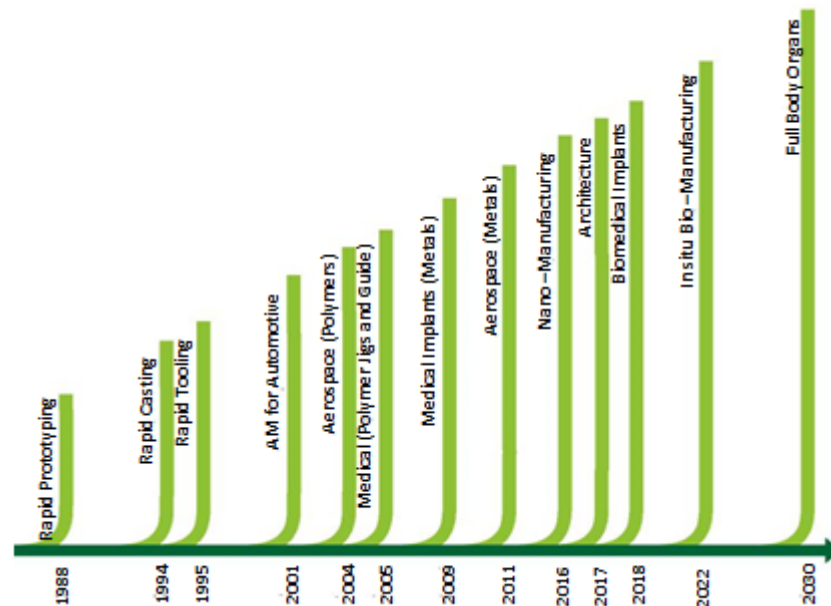


Figure 5: Predicted Additive Manufacturing Timeline from 1988-2030 [12]

4.3 Economies of Scale of Additive Manufacturing

Economies of scale are referred to as the bargain in the unit cost of production as the volume of production is increased. Economies of can be the cost reduction due to technological and management factors which can be internal to an organization or the effect of technology in an industry which is external to an organization[13, 14]. In economics, a distinction is made between fixed costs (e.g. an assembly line) and variable costs (inputs such as natural resources and labour). As volumes increase in a conventional manufacturing process, the cost for each unit of output declines since the fixed cost can be spread across more units. This is demonstrated by line A-B in the Figure 6[14]. The line C-D indicates Additive manufacturing technology where the cost of the first unit will be as expensive or cheap as the thousandth one. This implies that once you own a 3D printer, it can be regarded as a fixed cost, which in this case it is significantly smaller. The unit cost curve for AM therefore becomes almost a horizontal line, therefore making economies of scale much less important[14]

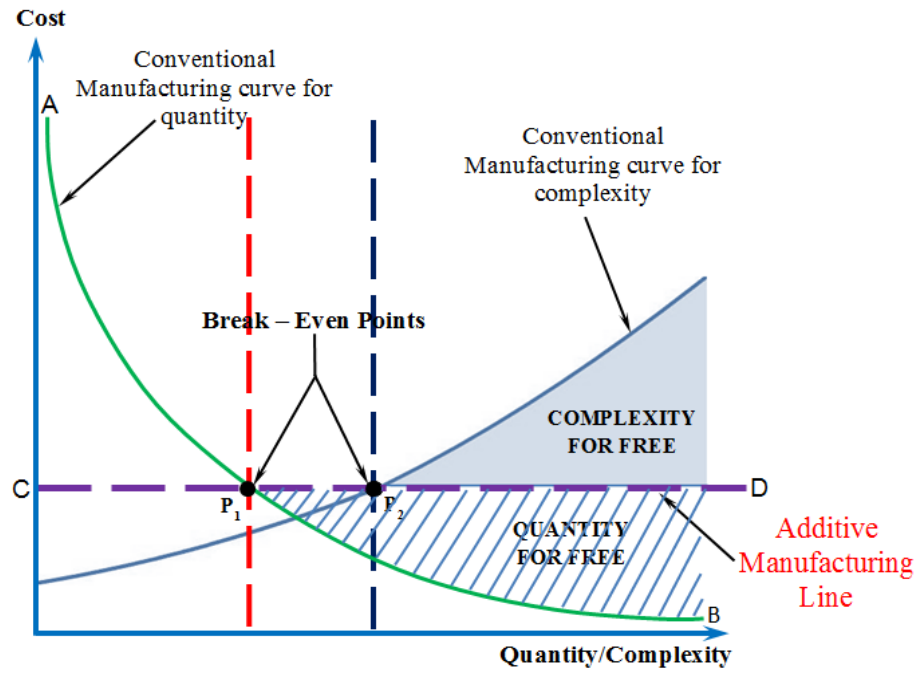


Figure 6: Economies of Scale of Additive Manufacturing [14]

5.1 Multi-Disciplinary Nature of AM Technology

Although there are limitations in the use of Additive Manufacturing Technology, it still possesses a wide range of multi-disciplinary culture of materials and application[15]. More research are been conducted for both more applications and materials used.

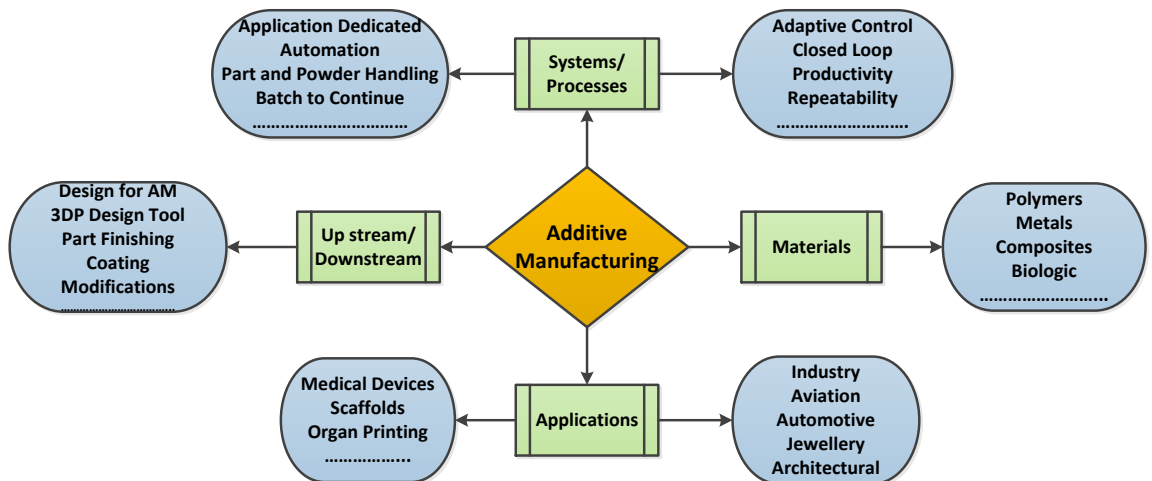


Figure 7: Block diagram showing the multi-disciplinary nature of AM technology [15]

5.2 Medical Applications

AM technology has gained grounds in the medical field even though there is more room for improvements. One opportunity is its use for medical devices for planning and conducting surgery and custom surgical implants[16]. Custom prosthetics and orthotics are other potential applications for AM which were relatively early uses of AM due to the ability to produce custom-fit parts for highly variable joints, amputated limbs, and cavities (for example, ears for hearing aids)[17]. What makes AM technologies even more appealing in medical applications is that they utilize medical imaging data obtained by Computer Tomography (CT) or Magnetic Resonance Imaging (MRI), almost directly for the production of customized patient specific parts[6].

Using AM for a custom implant offers several advantages such as making operation less complex, reducing operating time and the associated risk to the patient involved with being in surgery for so long. It also reduces the possibility of repeating a surgery that is needed because it cannot be done right the first time[18].

Figure 8 shows a model of 14-month's old child heart built in three pieces using a flexible filament printed at the School of Engineering at the University of Louisville. This took around 20 hours and cost US\$600 and allowed the doctors to better prepare for a successful operation[4].

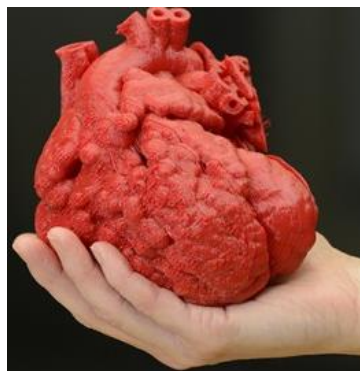


Figure 8: Additive Manufacturing Child Heart Model [4]

5.3 Aerospace and Aeronautic Applications

AM is used for making non machinable complex parts for direct use preferably in the aerospace and the medical industry because of its mostly dense parts and very good mechanical properties[19].

Aerospace and aeronautic components are critical parts which should be produced within very close tolerances to fulfil the high dimensional accuracy and surface finish. Also, when designing aerospace parts, producing of corners is avoided as much as possible to reduce stress concentration to the barest minimum and for this reason, critically chosen process should be used thereby making AM application more suitable[20].

AM technologies have proven to be a solution to parts complexities and therefore become the obvious choice for aerospace design as other forms of machining simply

cannot meet the required standards. Also, often the case that the material required cannot be processed by conventional means and is too expensive in regards to buy-to-fly ratio are not relevant when it comes to Additive Manufacturing as the ratio is greatly reduced to minimize cost[20]. Figures 9 and 10 shows some examples model aerospace parts produced using AM.



Figure 9: Wind Tunnel Model Tiltrotor [1]



Figure 10: Modelled Jet Engine [1]

5.4 Tooling Application

Figures 11 and 12[21] show sample of Additive Manufacturing or 3D printing used for the process of casting patterns for investment casting which is used to create a mold for use in metal casting.



Figure 11: Investment Casting Pattern [21]



Figure 12: 3D Systems CastForm PS Material [21]

5.5 Automotive Applications

Additive Manufacturing of automobile parts is a proven technology used by automobile engineers and designers to produce physical, tangible prototypes to work within design and testing. AM has been used to create a wide variety of parts in many materials, small and large automobile parts. Some examples of automobile parts produced by AM are Engine castings, engine parts, brakes, dashboards, handles, and knobs[22]. Figures 13 shows a turbocharger[22] and Figure 14 shows an engine block[23] all printed by AM technology.



Figure 13: AM Printed Turbocharger [22]

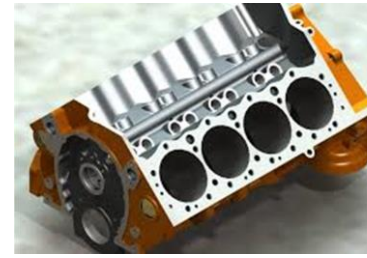


Figure 14: AM Printed Turbocharger [23]

5.6 Architectural Application of Additive Manufacturing

AM technology has made Architectural and Construction fields overcome the difficulty in viewing the interior design of a structure. It enables structures and components be printed, therefore allowing high complexity and customization, and allow material to be used only where it is specifically needed. It also enables structures to be built on-site, thereby eliminating long and long supply chain, hence, decreasing total cost of production[24].

Figure 15 a 3D printed scale model of INHOLLAND University with Stratasys Objet Eden350TM 3D Printer[25].



Figure 15: Scale model of INHOLLAND University [25]

5.7 Jewellery Application of AM

Many of the materials used for jewel making are expensive and therefore needs to avoid waste as much as possible. Even where wastes are re-used, re-processing tends to be energy expensive. Additive Technology Selective Laser Sintering (SLS) is associated to suitable powder metallurgy to enable metal components to be built in customize demand and without scrap for re-processing[26, 27]. Figure 16 shows some examples of jewels[28, 29] produced using SLS process of AM.

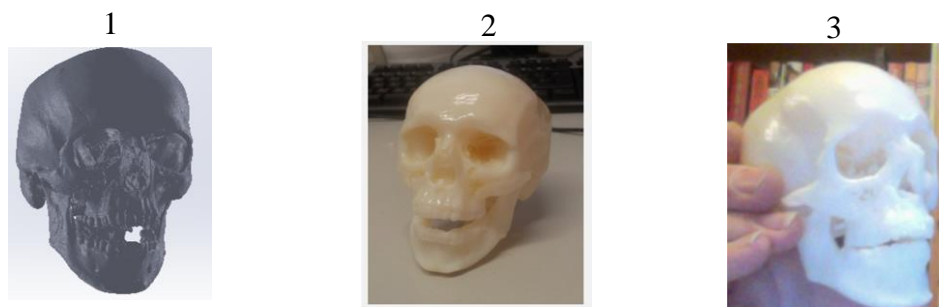


Figure 16: Metallic Bracelets and Necklaces Produced by SLS Process [28, 29]

6 Case Study at Northumbria University, Newcastle upon Tyne

6.1 Printed Skull

Figure 17 (1–3) shows a 3D printed skull at the Northumbria University 3D-Printing laboratory. The laboratory received the scanned data of the skull of the man in question who sustained a brain injury upon having a motor accident. The scanned data was saved in stl. file which was subsequently sent to the Objet 3D printing machine for printing. The figure 16 – stage 3 shows the printed model which took approximately 20 hours to complete the printing. The printed skull clearly shows the damaged part.

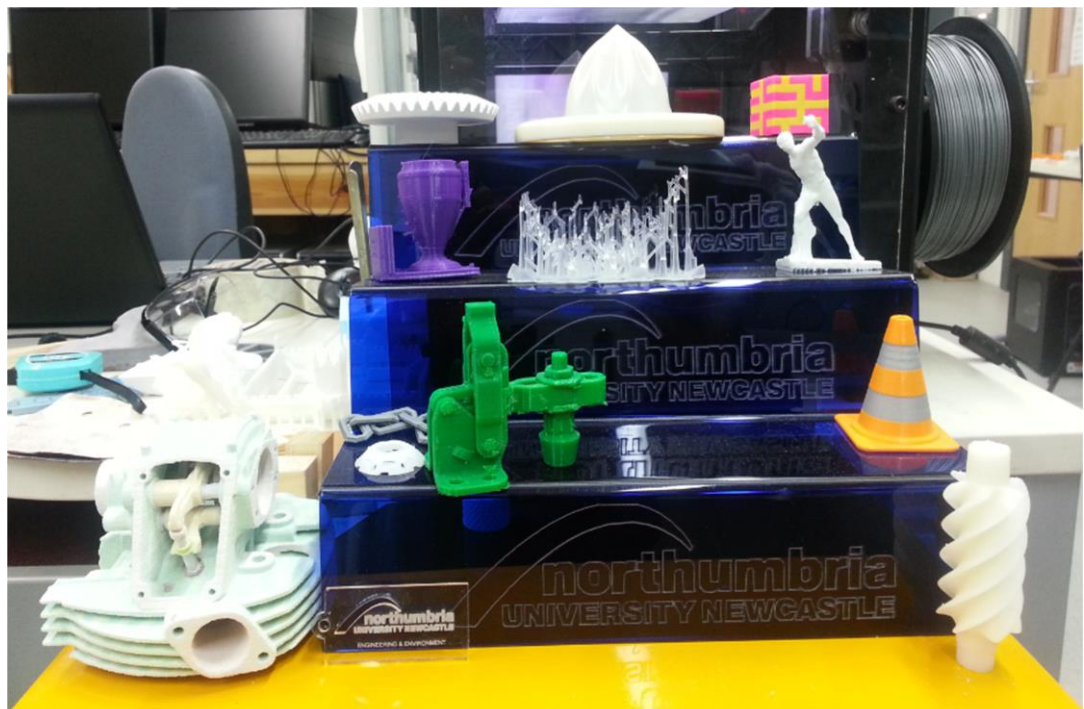


Stage	Activity
1	CT Scan Model (.stl file)
2	Printed Model Halfway Cleaned
3	Final Printed Model

Figure 17: Printed Skull at Northumbria University

6.2 Other Parts Printed at Northumbria University

Figure 18 shows models for several applications printed at Northumbria University using various types of 3D facilities.



Some Student Projects

Figure 18: Models Printed at Northumbria University

7. CONCLUSIONS AND FUTURE WORK

7.1 Conclusion

Additive Manufacturing technology has brought a remarkable revolution since its emergence in the global manufacturing field. The technology has tremendously helped

trim weeks, even months of design, prototyping and manufacturing time whilst avoiding costly errors and improving product quality. The problem of scrap disposal which is detrimental to the environment is eliminated and parts can be built on-site once the company can afford the machine and there is power supply. One of the major obstacles of AM technology is surface finish and material application which are critical to many engineering.

Many researchers are working tirelessly to overcome the weaknesses of the technology and it is therefore expected that even though it cannot fully replace the traditional production methods, it will strive to hit its target of printing full human organ by the year 2030. When AM is fully understood and utilised correctly, an impressive niche and cost saving are possible in the entire manufacturing world and beyond.

7.2 Future Work

The research team intends reviewing the past, current, and the predicted future development of the AM technology and conduct several tests on such material as Polyurethane (PU) which has not been printed by the technology to determine the suitability of its applications for further reduction of weight and cost. The problem of surface finish is another issue the research team hopes to tackle by incorporating a system to the existing AM technology to match with other machining processes such as CNC machining and grinding.

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NC1 Abstracts of Internal (Northumbria University) Conferences Presented

NC1.1 Research Conference – 2014

Title: Additive Manufacturing Technology Applications

Author: C. E. Oppon

ABSTRACT

Additive Manufacturing is a layer by layer process where one layer of a material is deposited on a previously deposited one until the final object is obtained. This is different from the traditional manufacturing where material is removed from a blank to obtain the required shape. The technology was originally used for Rapid Prototyping (RP) but now emerging as a full functional part process, taking a leading position in the manufacturing sector. As a result, several manufacturing companies are moving from or adding “analogue” to “digital” where a cost saving and design benefits are paramount as compared to traditional manufacturing. From a design standpoint, a part which is not physically possible in the past due to its complexity could now be achievable by the AM technology from polymer to metal and from engine block to precision prosthetics. This poster exhibits some of the recent progress made by some leading manufacturing industries and academicians. It also shows preliminary foaming experiments when varying the mixing ratios of Polyurethane (PU) materials in their applications for Additive manufacturing technology.

Keywords: Additive Manufacturing; Full Functional Part; Traditional Manufacturing; Polyurethane Foam

NC1.2 Research Conference – 2015

Title: Application of Additive Manufacturing Technology for Lightweight Medical Scaffolds using Polyurethane foam.

Authors: C. E. Oppon, P. M. Hackney, I. Shyha, M. Birkett

ABSTRACT

Additive Manufacturing (AM) is an innovative idea to fabricate complex, net-shaped components in successive layers. The technologies are used for rapid prototyping technique enabling short lead-times and design changes can easily be incorporated. By omitting extensive machining, material costs and scrap can be reduced, leading to a lower environmental impact with a good economic balance. The AM technologies offer the potential to fabricate organised tissue constructs to repair or replace damaged or diseased human tissues and organs. Using these techniques, spatial variations of cells along multiple axes with high geometric complexity in combination with different biomaterials can be generated but still with limited material application. Most of these tissue constructs are one off which is among the major positive characteristics of AM. Even though Polyurethane foam has the properties to support soft tissues (e.g. breast implants), and less expensive compared to other materials, its potentials have not been fully exploited by AM technology. This presentation reviews the economic balance of AM and reports on the effects of mechanical properties of polyurethane foam by

varying the mixing ratio and pre-heated temperature of the main constituents (polyol and diisocyanate) in its application by AM to manufacture lightweight medical scaffolds for implants.

Keywords: Additive Manufacturing, Polyurethane Foam, Medical Scaffold, Biomaterials

NC1.3 Three Minutes (3MT) Presentation Competition

Abstract

Additive Manufacturing also known as 3-D Printing refers to a number processes used in manufacturing physical models, prototypes or end use products layer by layer directly from three-dimensional Computer Aided Design data. Additive manufacturing is growing fast in many applications including medical field due its fast production of intricate parts in single batches. This fast growth has caught the interests of many researchers into more materials applications and better understanding of the possibilities. Additive Manufacturing bids designers and manufacturers the opportunity to create organic custom parts with biocompatible materials; one such of these materials is Titanium. The application of AM in the medical field includes: surgical aids, medical tools, orthopaedic implants, and dental prosthetics to be used in humans. A lot of materials have been employed for medical implants and scaffolds, including polyurethane (PU) foam which has been used to coat silicone gel breast implants. The versatility of PU as a construction material, its physical properties and biocompatibility makes it suitable for medical applications. It is therefore important for designers and manufacturers to investigate the appropriate usage of PU in order to influence these versatile properties. With the extensive use of PU for various applications, Additive Manufacturing process has not been used in its dispensing. This paper therefore investigates the properties of PU foam for lightweight medical scaffolds applications and validates its production using an Additive Manufacturing process.

Keywords (up to three): Additive Manufacturing, Three-Dimensional Printing, Layer Manufacturing